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CONTENTS

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NOTICE TO MEMBERS AND SUBSCRIBERS

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

COMMUNICATIONS

The Effect on Wool of Boiling in Aqueous Solutions
II—Solutions of Ammonium Salts with and without Ammonia

R. V. PERYMAN

The pH values at 100°c. obtained by extrapolation from measurements on dilute aqueous solutions of ammonium sulphate, acetate, (diammonium) phosphate, chromate, and chloride at temperatures ranging from 18° to 80°c. agree approximately with the pH values at 100°c. calculated from the published dissociation constants of the acids, ammonium hydroxide, and water. It follows that pH measurements on the solutions at room temperatures cannot, without other data, be relied upon to indicate their pH values at 100°c. Ammonium salt solutions containing added ammonia can have pH values ca. 2 units lower at 100°c. than at 18°c. Ammonium sulphate–ammonia solutions of alkaline pH values ≯ 8 when measured at 18°c. have acid pH values < 6 at 100°c. without loss of ammonia. Metachrome mordant solutions with room-temperature pH values ca. 6·7–8·7 are at 100°c. buffered at ca. pH 6·7.

Wool yarn, boiled for 3 hr. in the ammonium salt and ammonia solutions (excluding chromate and chloride) at controlled pH values and at concentrations simulating commercial dyeing, gives degrees of modification, as measured by wet breaking load and content of disulphide sulphur, in fair agreement with the salt contents of the solutions and the pH values at 100°c. but not with the pH values at room temperature.

INTRODUCTION

Ammonium sulphate and acetate are commonly used as assistants in the dyeing of wool, and ammonia also may be added at the commencement of dyeing. Treatment of wool with solutions of ammonia at temperatures a few degrees below the boil is used for stripping acid dyes from wool and for shade correction; the liquor may also contain salts. Noble [1] has advocated the use of mono-ammonium phosphate as an alternative to ammonium sulphate and acetate for better pH control of the dye liquor and Pacific Mills [2] have suggested diammonium phosphate for pH control under slightly alkaline conditions.

Whilst a great deal of attention has been given to the use of ammonia and ammonium salts as a means of controlling dye absorption, comparatively little study has been made of their effect on the physical and chemical properties of wool. With the object of obtaining such information, the procedure adopted in Part I [3] has been applied in a modified form using ammonium salt and ammonia solutions.

EXPERIMENTAL

In the usual methods of dyeing, the influence of ammonium salts depends in part upon acid liberated by the volatilisation of ammonia, but loss of ammonia is prevented in the modern com-
pletely enclosed machines. Both types of treatments are difficult to simulate on a laboratory scale, though the second can be approached by an open apparatus in which lost ammonia is replaced by additions of aqueous ammonia at frequent intervals. The latter procedure has been adopted in the following experiments and, with the exception of certain acidic solutions which required small additions of acid, has been the means of maintaining constant pH values.

As in Part I [3], 90-g. batches of yarn from the same lot of 64s wool were boiled for 3 hr. (after bringing to the boil in 50 min.) in a Longclose laboratory model package-dyeing machine using a liquor ratio of 67 : 1, the pH of the liquor, measured on samples cooled to room temperature, being controlled by small additions of ammonia or of the appropriate acid. After final rinsing, the pH of the liquor in equilibrium with the yarn was adjusted to 6–7.

From the experience gained in Part I [3] it was considered that, for the purposes of the present study, changes in the wool could be evaluated sufficiently accurately by measurements of the wet-bundle breaking load and the disulphide sulphur content of 2/14s yarn. Improvements in the precision of the results have been achieved by (a) prior calibration of the breaking-load test

samples with a dielectric-type yarn-count meter, and (b) disulphide sulphur determinations with the aid of a Unicam model SP 600 spectrophotometer using a wavelength of 880 mμ. and Folin's [4] uric acid reagent.

Estimation of pH Values at 100°C.

Most investigators of the action of aqueous solutions on wool have made their pH measurements at or near room temperatures because of experimental difficulties at higher temperatures. As is implicit in the definition of the pH scale, the interpretation of pH values measured at room temperature but referring to solutions at higher temperatures is necessarily subject to reservations. That salts of pseudo-bases may behave in an exceptional manner seems to have escaped notice but is suggested by the curves of Hannay, Major, and Pickin [5] showing some relationships between the pH value and temperature of measurement of metachrome mordant solutions. A clarification of the temperature–pH relationships of ammonium salt solutions therefore seems essential to the purpose of the present paper and has been carried out in the following way.

By means of a high-temperature glass electrode, manufactured by Messrs. George Kent Ltd., pH measurements have been made at 40°, 60°, and 80°C. on a range of ammonium salt solutions, and the pH values at 100°C. found by graphical extrapolation. The solution for pH measurement was contained in a rubber-stoppered 100-ml. glass tube connected by a glass siphon to an open expansion tube, also containing some of the solution, into which dipped a glass hook tube full of saturated potassium chloride, which in turn was connected to a calomel electrode with polythene tubing. The glass electrode was fitted through the rubber stopper, as was the thermometer, which, by having a sliding fit, also served as a stirrer. The glass electrode vessel was immersed in water in a 400-ml. tall-form beaker, which was wound with a low-wattage coil of resistance wire supplied through a transformer. With the exception of the calomel electrode, which was kept on the bench in a Dewar flask at room temperature, the remainder of the electrode system was fitted into a water-jacketed oven regulated at slightly above the temperature selected for the measurement. Thus, though a temperature gradient existed in the saturated potassium chloride bridge solution leading from the oven to the calomel electrode, this was constant for each standardisation of the electrode system, and thermal effects on the calomel electrode were thus avoided. The glass electrode was connected by shielded cable to a Cambridge Instrument Co. pH meter, the temperature-compensating dial of which was set at 25°C. Corrections for pH readings at other temperatures were then calculated from the formula—

$$pH = \frac{(t - 25)(pH_r - pH_s)}{t + 273}$$

(t°C. = temperature of measurement; pH_r = reading on pH meter; and pH_s = pH of the buffer solution used for standardising at t°C.).

As the high-temperature electrode was not suitable for measurements at room temperature, these were made with a Morton cell and Cambridge Instrument Co. pH meter after quickly transferring the solution via the siphon from the high-temperature electrode vessel to a flask which was immediately stoppered and cooled. In some instances the solution was cooled in the electrode vessel before transference. As it was rarely possible, over a series of temperatures, to maintain a solution exactly at chosen pH values when referred to room temperature, small corrections, obtained from repeat experiments at similar pH values, were necessary in some cases in order to plot the results.

The glass electrodes were standardised at each selected temperature of measurement with buffer solution, 0·025 M. with respect to both potassium dihydrogen phosphate and disodium hydrogen phosphate (AnalaR grades) and prepared from water free from carbon dioxide. The pH values of this buffer at temperatures up to 60°C. are given by Bates and Acree [6]. In the absence of any generally accepted pH value for the buffer solution at 80°C., the value at this temperature was taken as 6·88 by extrapolation above 60°C. of these authors' results. Some preliminary results of Bates [7] for temperatures up to 95°C. support the choice of this value. This buffer solution, together with values at 80°C. similarly obtained for 0·05 M. potassium hydrogen phthalate [8] and 0·01 M. borax [9] solutions, were used to check the response of the glass electrode.

The ammonium salt solutions chosen for measurement represented those normally used in commercial dyeing; but, to reduce possible complications from impurities, the salts and ammonia were of AnalaR quality and the solvent, unless otherwise stated, was distilled water which had been boiled for 20 min. and allowed to cool in an atmosphere freed from carbon dioxide.

Most solutions contained only single salts, but it was thought desirable to have some results for mixtures such as are used in practical dyeing, e.g. with metachrome mordant. Those given in Table II have been measured with the above apparatus; but two additional series of measurements on metachrome mordant solutions (Fig. 1 and 2) have been made with a Kent Mark II (glass electrode) Universal pH Recorder fitted with a dip-type electrode unit, which was immersed in 10 litres of solution in the small package-dyeing machine. Measurements were made between 45° and 85°C., and small quantities of ammonia were added to maintain constant the pH values when measured at 20°C. The measurements at room temperature were made with the Cambridge pH meter after cooling the test solution in a stoppered flask, the final sample being taken when a steady value was shown on the chart of the recorder. As a further aid to accuracy, the Kent pH meter was standardised at 50°C., with the phosphate buffer already described, for measurements between 45° and 60°C., and at 80°C. for measurements between 70° and 85°C. The first series of solutions measured contained metachrome mordant at a

concentration corresponding to a "short" dye liquor at the commencement of dyeing, and the second series corresponded to the same dye liquor near the end of dyeing, i.e. when 80% of the chromate would have been exhausted.

RESULTS

The results of the pH measurements on single salt solutions, which have mostly been made in duplicate, and their extrapolation to 100°c., together with some results obtained by calculations from the formula of Eeckhout [10], are given in Table I. The results for metachrome mordant solutions, given in Table II and Fig. 1 and 2, are single measurements at each temperature. The results showing the effect of the boiling treatments on wool are given in Table III.

DISCUSSION

It will be observed from Table I that at 100°c. and without loss of ammonia the pH values of the solutions of single salts tend to have a value characteristic of the salt concerned, this value being largely independent of the concentration of the salt within the range studied, a feature to be expected with solutions of salts whose acid and base are both weakly dissociated, but which can hold only roughly for ammonium sulphate solutions at 100°c. The pH values of ammonium chloride solutions will, of course, depend on the con-

centration. Good agreement has, moreover, been found between these experimental values and those calculated from Eeckhout's formula using dissociation constants quoted in the literature. The unusually large decrease with rise of temperature in the second dissociation constant of sulphuric acid is noteworthy, and accounts for the fact that the fall in the pH value at 100°c. is lower for the ammonium sulphate solution than for the ammonium chloride solution of equivalent strength. It would appear that this property of ammonium chloride could prove useful for dyeing at pH values about 0·7 unit lower than those given by ammonium sulphate.

If the pH value of an ammonium salt solution measured at 18°c. is raised by the addition of ammonia, the value for the ammonia–ammonium salt solution at 100°c. is not more than ca. 2 pH units lower than its value at 18°c., whilst the neutral point of water at 100°c. is only ca. 1 pH unit lower than its value at 18°c. (It is realised that the presence of salt in the amounts used in the experiments will further depress the neutral point of water at 100°c., but this effect is not considered sufficiently large to be of importance in interpreting the results.) That the pH value of ammonium salt–ammonia solutions can shift to the acid side of neutrality is shown by the ammonium sulphate–ammonia solution which has

TABLE I

Relation between pH and Temperature of Ammonium Salt Solutions

Soln.	Composition	Concn. of NH₄ Salt (g./litre)	pH at Room Temp. (°C.)	pH at (°c.) 40°	pH at (°c.) 60°	pH at (°c.) 80°	pH at 100°c. By Extrapolation	pH at 100°c. Calc.*
1	$(NH_4)_2SO_4$	6·0	5·49 at 20°	5·34	5·20	5·03	4·9	4·9
2	$(NH_4)_2SO_4 + NH_3$	6·0	6·37 at 19·5°	5·91	5·57	5·23	4·9	—
3	$(NH_4)_2SO_4 + NH_3$	6·0	7·39 at 19·5°	6·85	6·38	5·92	5·5	5·5
4	$(NH_4)_2SO_4 + NH_3$	6·0	8·55 at 21°	8·00	7·52	7·02	6·6	6·6
5	$(NH_4)_2SO_4 + NH_3$	0·4	8·56 at 21°	8·05	7·52	7·02	6·5	6·6
6	$(NH_4)_2SO_4 + NH_3 + NaHCO_3$ (0·5 g./litre)	6·0	8·30 at 17·5°	7·68	7·22	6·83	6·5	—
7	$(NH_4)_2SO_4 + NH_3 + NaHCO_3$ (0·5 g./litre)	0·4	8·50 at 17·5°	7·92	7·57	7·35	7·3	—
8	$CH_3·COONH_4$	3·5	6·96 at 20°	6·77	6·60	6·38	6·2	6·2
9	$CH_3·COONH_4 + NH_3$ ...	3·5	7·38 at 18°	7·02	6·68	6·42	6·2	—
10	$CH_3·COONH_4 + NH_3$ ...	3·5	8·41 at 18°	7·80	7·26	6·86	6·5	6·4
11	$(NH_4)_2HPO_4 + NH_3$ ...	6·6	8·48 at 18°	7·96	7·62	7·35	7·2	7·2†
12	$(NH_4)_2HPO_4 + H_3PO_4$ ...	6·6	7·52 at 19°	7·40	7·31	7·14	7·1	—
13	$NH_4H_2PO_4 + NH_3$ ...	5·7	6·26 at 20°	6·24	6·23	6·19	6·2	—
14	$(NH_4)_2Cr_2O_7 + NH_3$ ...	2·0	6·54 at 20°	6·56	6·57	6·58	6·6	—
15	$(NH_4)_2Cr_2O_7 + NH_3$ ...	2·0	7·12 at 20°	7·04	7·00	6·87	6·8	6·8†
16	NH_4Cl	5·4	5·27 at 18°	5·02	4·79	4·50	4·3	4·2
17	Water only	—	7·12‡ at 18°	6·77‡	6·51‡	—	—	6·1‡

*From the formula of Eeckhout [10] using the following constants—

Acetic acid	... ...	pK_a =	4·95 Noyes and Cooper [11]
Ammonium hydroxide...		pK_b =	4·57 Noyes and Kato [12]
Chromic acid	...	pK_{2S} =	6·49 Neuss and Riemann [13] (value at 25°c. assumed for 100°c.)
Phosphoric acid	...	pK_{2S} =	7·31 Bates and Acree [14] (by extrapolation)
Sulphuric acid	...	pK_{2S} =	2·74 Noyes and Eastman [15]
Water	... ...	pK_w =	12·24 Heydweiller [16]

†For the diammonium salt only (refers to $(NH_4)_2CrO_4$ for Solution No. 15).

‡Values of ½ pK_w after Harned and Hamer [17] (at 100°c. after Heydweiller [16]).

a pH value of 7·39 at 19·5°c. and 5·5 at 100°c. (Table I, No. 3). The reverse case of a shift from an acid to an alkaline reaction with rise of temperature is to be expected when a solution maintains pH values between 6·1 and 7·1 as the temperature rises whilst the neutral point changes as usual from pH 7·1 to 6·1. This occurs with mixtures of monohydrogen and dihydrogen phosphates as well as with mixtures of chromates and dichromates, i.e. with partly neutralised solutions at pH 6·1–7·1 of acids with pK values of ca. 6–7·5. Examples of this behaviour are to be found in the mixed ammonium chromate and dichromate solution (Table I, No. 14), the mixed ammonium phosphate solution (No. 13), and also in the phosphate buffer solution used as the reference standard.

As would be expected from a salt of an acid and a base of almost equal strengths, the change in the pH value of the ammonium acetate solution (No. 8) follows approximately that of the neutral point of water but, owing no doubt to the dissociation constant of acetic acid falling a little more at 100°c. than does that of ammonia, ammonium acetate solutions react slightly alkaline at 100°c.

Solutions No. 6 and 7 were chosen to simulate dye liquors containing sodium carbonate from alkaline wool and carbon dioxide from industrial water. It can be seen that, of the two concentrations of ammonium sulphate, the higher concentration has been effective in swamping the effect of alkali, whereas in the other, in which near chemical equivalence was reached, a much smaller change in pH value has occurred, the behaviour resembling that of a mixed sodium and ammonium bicarbonate solution.

It is thus evident that room-temperature pH measurements of ammonium salt solutions with or without excess ammonia cannot be used to indicate their pH values at 100°c. without taking into account the effect of the anions present. This is especially true for alkaline solutions, and is to be

expected from conventional concepts of buffer solutions; but to understand the shift from alkaline to acid reaction with rise of temperature, as shown with ammonium sulphate–ammonia solutions of pH 7–8 at room temperature, it is convenient to employ the Lowry–Brönsted [18] theory of acids and bases. The ammonium sulphate–ammonia solution will then be seen to contain the acids NH_4^+, H_2O and the bases NH_3, OH^-, SO_4^{2-}, H_2O, its pH value in the range near and above neutrality being mainly controlled by the dissociation of the acid—

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$
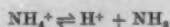
and of water. The dissociation constant of the ammonium ion is, however, related to its basic dissociation constant by—

$$\frac{K_w}{K_b}$$

where K_w is the ionisation constant of water. Since K_b has only a small temperature coefficient, the acidic dissociation constant of the ammonium ion varies almost entirely as K_w. Thus a fall in pK_w from 14·23 at 18° to 12·24 at 100°c. can be the cause of a fall of ca. 2 pH units in a solution of ammonium salt containing excess of ammonia. On this basis it appears reasonable to calculate pH values of ammonium salt–ammonia solutions at 100°c. from measurements at 18°c. by subtraction of 2 pH units, provided that their pH value at 18°c. is greater by 2 units than that of the salt alone at 100°c.

Fig. 1 and 2, giving respectively the results for solutions representing metachrome dye liquors at the beginning of dyeing and after partial exhaustion of chromate, show that above ca. pH 8·7, measured at room temperature, their behaviour is similar to that of ammonia–ammonium sulphate or acetate solution, but below about pH 6·7 the chromate controls the pH almost completely in the unexhausted liquors and to a lesser degree in the liquors which are 80% exhausted of chromate. It
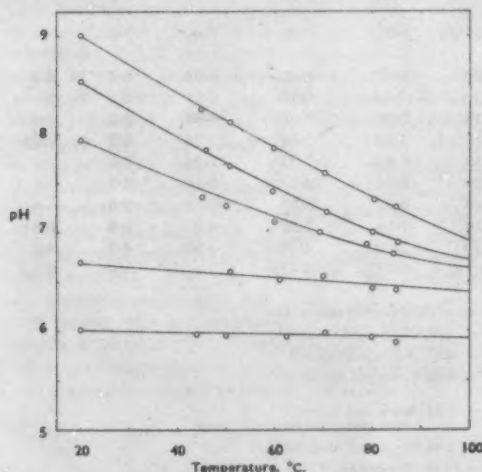
FIG. 1—Unexhausted Metachrome Liquor (4·44 g. $(NH_4)_2SO_4$ + 2·22 g. K_2CrO_4 per litre of tap water + NH_3 or H_2SO_4)
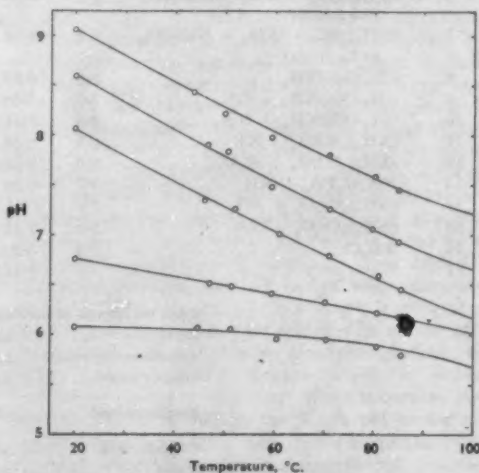
FIG. 2—Partly Exhausted Metachrome Liquor (4·44 g. $(NH_4)_2SO_4$ + 0·44 g. K_2CrO_4 per litre of tap water + NH_3 or H_2SO_4)

TABLE II
Metachrome Mordant and Dye Solutions

Soln.*	Composition		Concn. (g./litre)	pH† at 20°c.	pH at 100°c.
A	$(NH_4)_2SO_4$ ...	...	6		
	Na_2SO_4	...	10	7·44	6·7
	K_2CrO_4 ...	...	3		
B	As A ...	...	—	8·56	6·7
C	$CH_3 \cdot COONH_4$	...	3·5	7·46	6·8
	K_2CrO_4 ...	...	3		
D	As C ...	...	—	8·36	6·8
E	$(NH_4)_2SO_4$ ...	...	2·67		
	K_2CrO_4 ...	...	1·33	8·17	6·7
	Na_2SO_4 ...	...	2·5		
	Dye (a)‡ ...	...	4		
F	As E but Dye (b)‡ ...		—	8·06	6·7
G	As E but Dye (c)‡ ...		—	8·05	6·7

* Boiled-out tap water was used in solutions E, F, and G.
† Adjusted initially by the addition of ammonia or sulphuric acid (acetic acid for solution C).
‡ Dyes used— (a) Solochrome Brown MOS (ICI), 4 g./litre
(b) Solochrome Brown RH 125 (ICI), 3·2 g./litre
(c) Metachrome Brown B (Br), 4 g./litre.

thus seems that metachrome liquors of conventional formula are able to produce a slightly acid reaction only when nearing exhaustion, and it is further to be observed that unexhausted metachrome dye liquors having room-temperature pH values of ca. 6·7–8·7 have the same pH value of ca. 6·7 at the boil. The common pH value, 6·7, is most clearly shown in Table II, which is a record of measurements of higher accuracy than those obtained with the industrial type of pH meter. Unexhausted liquors having pH values above ca. 8·7 at room temperature can therefore be regarded as unnecessarily alkaline. Metachrome dye liquors of the same pH value but containing different amounts of metachrome mordant will differ, however, in their degree of attack on wool, because, as shown in Part I[3], increased attack in alkaline solutions is promoted by an increase in salt content. Thus significant amounts of alkali damage are to be expected when dyeing deep

colours with dyes requiring the maximum amount of metachrome mordant. For the same reason the addition of Glauber's salt to metachrome baths should be avoided.

In the light of the foregoing, the addition of ammonium phosphate to metachrome dye liquors appears to suffer from the disadvantage that, when an alkaline reaction is necessary to keep dye in solution in the freshly made dye liquor, higher pH values, with consequent risk of alkali damage to wool, are obtained at the boil than with the ammonium salts of sulphuric and acetic acids. In general, caution should be exercised in the addition to dye liquors of acids (or their salts) with pK values greater than about 6·5.

From Table III it is seen that, as already shown in Part I[3], there is good correlation between wet breaking load and disulphide sulphur content within the limits of error of the methods. If the degrees of fibre modification are compared at equal pH values measured at 18–20°c., e.g. treatments No. 4 and 11, or No. 3 and 7, wide differences are found; but if the pH at 100°c., as derived from Table I, is used as the basis of comparison, it is then apparent that equal degrees of modification at equal pH values, within the limits of error, are obtained, e.g. in treatments No. 7 and 8.

At first sight, anomalous results appear to have been obtained from (a) treatments No. 6 and 12, (b) treatments No. 8 and 9, and (c) treatments No. 5 and 10. These can be explained, since in (a) treatment No. 12 contained no salt, whereas the wool in No. 6 was subject to alkali attack caused by salt as shown in Part I[3]; and in both (b) and (c) No. 8 and 5 were subjected, in the 50 min. used in raising the bath to the boil, to considerably higher pH values than in the treatments with the solutions containing phosphates, which have been shown to maintain relatively uniform pH values below 7·2 over the temperature range.

The practice of entering at or near the boil in dye liquors containing ammonium sulphate and

TABLE III
Results of Tests on the Yarn

No.	Treatment Liquor Composition*	pH at (°c.) 18–20°	pH at (°c.) 100°†	Breaking Load of Wet Bundle Mean‡ (lb.)	C.V.§ (%)	(% of Control)	Disulphide S Content (%) On Dry Wt.	On Control
	Control	—	—	1·82	5·3	100	3·09	100
1	$(NH_4)_2SO_4$	5·2–5·1	4·9	1·57	3·7	86·3	3·07	99·3
2	$(NH_4)_2SO_4 + NH_3$ ...	7·5–6·6	5·5–4·9	1·54	6·5	84·6	2·93	94·8
3	$(NH_4)_2SO_4 + NH_3$ ...	6·5–6·8	4·9	1·55	5·5	85·2	3·06	99·0
4	$(NH_4)_2SO_4 + NH_3$ ...	7·9–8·0	5·9–6·0	1·45	4·7	79·7	2·80	90·6
5	$(NH_4)_2SO_4 + NH_3$ ...	8·7–8·6	6·7–6·6	1·28	6·8	70·3	2·53	81·8
6	$(NH_4)_2SO_4 + NH_3$ ...	9·0	7·0	1·25	7·5	68·6	2·34	75·7
7	$CH_3 \cdot COONH_4$ ...	6·7–6·0	6·2	1·44	5·6	79·2	2·69	87·0
8	$CH_3 \cdot COONH_4 +$'NH_3 ...	7·8–8·0	6·2	1·43	3·3	78·6	2·59	83·8
9	$NH_4H_2PO_4 + NH_3$ ...	6·3–6·2	6·2	1·50	5·6	82·4	2·82	91·2
10	$(NH_4)_2HPO_4 + H_3PO_4$ ...	6·6–6·9	6·6–6·9	1·41	6·8	77·5	2·63	85·0
11	$(NH_4)_2HPO_4 + H_3PO_4$ ...	7·7–8·0	7·1–7·2	1·25	6·8	68·6	2·37	76·7
12	NH_3 in dist. H_2O ...	8·9–9·1	6·9–7·1	1·41	6·7	77·5	2·54	82·2

*Concn. of NH_4 salt 2·5 g./litre in all cases.
†The pH values at 100°c. are derived from Table I.
‡Mean of 25 tests.
§C.V. = Coefficient of variation.

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ammonia, as in Goodall's method [19], can be seen to lead to less alkali damage to wool than entering at lower temperatures, provided that the amount of ammonia is kept low.

SUMMARY OF CONCLUSIONS

(1) Measurements at room temperatures of pH values of ammonium salt solutions with or without added ammonia cannot, without further information, be relied upon to indicate their pH values at 100°c.

(2) The pH values at room temperatures and 100°c. of simple dilute ammonium salt solutions can be calculated approximately from published dissociation constants using Eeckhout's formula [10], and a simple extension of the formula can be used to calculate pH values at 100°c. of dilute ammonium salt–ammonia solutions when their pH values at room temperatures are known.

(3) Measurements of the pH values of the solutions at 40°, 60°, and 80°c. with a high-temperature glass electrode and extrapolation of the results to 100°c. have given results in fair agreement with the calculated values.

(4) The pH measurements have shown that, for the addition of the following salts to dye liquors from which ammonia is *not* permitted to escape, the following conditions may be expected—

(a) Ammonium sulphate–ammonia solutions of pH less than ca. 8·0 measured at room temperature produce slightly acid pH values at 100°c.

(b) Ammonium acetate solutions, with or without added ammonia, do not produce acid pH values at 100°c.

(c) Ammonium phosphate–ammonia solutions of pH values greater than ca. 6·1 measured at room temperature produce alkaline pH values at 100°c.

(5) Unexhausted metachrome mordant solutions at pH values of ca. 6·7–8·7 when measured at room temperature have been shown to have a common pH value of ca. 6·7 at 100°c.

(6) Wool when boiled in solutions of similar strength of ammonium sulphate, acetate, and phosphate, with or without the addition of ammonia, has been found to suffer degrees of modification which correlate well with the pH of the solution at 100°c. but not with pH values measured at room temperature.

*   *   *

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The Preparation and Properties of Regenerated Cellulose containing Vinyl Polymers

II—Staining, Swelling, and Stiffness Characteristics

G. LANDELLS and C. S. WHEWELL

Staining and swelling tests have confirmed that vinyl polymers may be readily deposited inside viscose rayon filaments and that different degrees of penetration are obtained depending on the properties of the monomer employed. Vinyl polymers increase the stiffness of viscose rayon filaments, and as increasing amounts of polymers are deposited internally the filaments become increasingly distended. About 8% of polymer may, however, be introduced without causing any change in the diameter of the fibres.

In Part I of the present investigation [1] evidence has been provided that, under suitable conditions, considerable amounts of vinyl polymers derived from both readily soluble and almost insoluble monomers can be deposited in regenerated cellulose. It is to be expected that fibres containing polymers would have physical properties different from those of untreated fibres, and the present account deals with an examination of this aspect of polymer deposition.

Measurements of wet stiffness have been made to confirm the deposition of polymer and to determine the relative degrees of hardening of viscose rayon monofilaments given by the different polymers. Staining and swelling tests have been used to provide visual evidence of the location of the polymers relative to the cellulose. Observations that polymer deposition caused an increase in fibre diameter have been confirmed by precise measurement.

Experimental

MATERIALS

Viscose rayon monofil (Courtaulds Ltd.) approx. 0·05 cm. in diameter, in which vinyl polymers had been deposited, was found to be very suitable for the staining, swelling, and wet stiffness measurements; while viscose rayon yarn (Courtaulds Ltd.) of 980 denier, 178 filaments, was employed in the experiments dealing with fibre diameter. The methods employed for depositing polymers inside were those described in Part I [1]. The sample numbers denoting the test specimens are those used in Part I, and this enables the method of depositing polymer in any specimen to be correlated with the test results.

1. STAINING

Most of the stains suggested for locating condensation resins are not effective on vinyl derivatives, but a solution of iodine (5%) in aqueous potassium iodide solution (10%) was found to be most satisfactory. This stains both vinyl polymers and cellulose, but on washing, the colour is readily removed from the cellulose. The technique consisted, therefore, in immersing the test specimens, and a sample of viscose rayon monofil, in the stain for 24 hr., and then rinsing in water until the colour was removed from the control. Material containing polymer remains stained, and the extent of penetration may be determined by cutting cross-sections.

2. CUPRAMMONIUM HYDROXIDE SWELLING TEST

The rate of dissolution or swelling of thin discs of viscose rayon monofil containing polymer was assessed by placing them on a microscope slide and introducing cuprammonium hydroxide (15 g. Cu + 200 g. NH$_3$ per litre) under the cover slip. Several changes of the cellulose solvent were introduced. Alternatively, short lengths of monofil were similarly examined in a small glass cell.

3. WET STIFFNESS TEST

Since the diameter of the monofil was ~0·05 cm., there was no need to adopt the refined techniques developed for fine fibres. Test specimens were soaked in distilled water for at least 24 hr. at room temperature before being clamped firmly (finger tightness) between metal jaws and cut to give a cantilever 2·5 cm. long. The location of the tip was determined with a travelling microscope, and the filament was then loaded at the end by a glass hook which weighed 50 mg. The deflection was measured to the nearest 0·005 mm. approx. 5 sec. after applying the load. In general, measurements on ten different filaments were taken to assess the effectiveness of a particular polymer deposition.

4. MEASUREMENT OF FIBRE DIAMETER

Viscose rayon yarn treated in the form of small hanks was unravelled, and a random sample of fibres taken. The fibres, each approx. 5 cm. long, were fixed at the ends to microscope slides by a small amount of adhesive (Perspex (ICI) in chloroform). About four turns of twist were introduced and the fibres were conditioned for at least 24 hr. at 65% R.H. and 22·2°c. Fibre diameters were measured at regular intervals along the fibres employing a microscope set to obtain a magnification of 570× and fitted with a micrometer eyepiece. Thirty readings were taken on each of fifty fibres, thus providing sufficient data to enable the results to be treated statistically.

Results

1. STAINING

When viscose rayon monofil is placed in a solution of iodine, it readily becomes stained throughout the structure as shown by cutting cross-sections. Specimens of viscose rayon monofil containing methyl methacrylate polymer are initially not quite so readily stained, but ultimately they also become completely penetrated. On placing completely stained specimens of untreated

and treated viscose rayon in distilled water, differences in behaviour are striking. The untreated specimens lose iodine progressively from the surface, and eventually the stain is completely removed, whereas viscose rayon containing methyl methacrylate polymer retains iodine tenaciously near the outer surface even when iodine has been completely desorbed from the central region. These differences are shown clearly in Fig. 1 and 2. The specimen (Sample No. 4) employed to give Fig. 2 was one containing 28·7% of methyl methacrylate polymer, which, as shown by the stain, only partly penetrates the comparatively thick monofil. For purposes of comparison monofil was coated with a preformed polymer of methyl methacrylate from a solution in chloroform (prepared by dissolving Perspex sheet), dried, and submitted to the staining test. The monofil behaved as untreated viscose rayon, but a thin surface film of polymethyl methacrylate remained highly stained and did not adhere firmly to the viscose rayon filament. This is shown clearly in Fig. 3, which is in marked contrast with Fig. 2, where the polymer is located internally.

Viscose rayon monofil containing polystyrene shows an even more limited degree of penetration. This is shown by the sample illustrated in Fig. 4. This specimen (Sample No. 14) contained 21·7% of polystyrene, which had been deposited by the thermal polymerisation method. Although some difficulty was encountered in cutting a good section because of the stiffness of the fibres, it seems likely that disruption of the outer regions, which may be observed in Fig. 4, is not due to sectioning but is brought about by the growing polymer. Individual monofils showed a tendency to be warped owing to polystyrene deposition.

Complete permeation of the monofil by a polymer, shown by staining throughout the cross-section, was obtained, however, in the case of acrylonitrile. Specimens of monofil (Sample No. 28) containing 59·6% of polyacrylonitrile retained iodine tenaciously during desorption, and remained intensely stained after three days in distilled water.

This staining test may be of fairly general application in determining the location of vinyl polymers in viscose rayon, although it should be noted that it was not effective with viscose rayon (Sample No. 38) containing 45·7% of polymethacrylamide.

2. SWELLING IN CUPRAMMONIUM HYDROXIDE

When untreated viscose rayon monofil is placed in cuprammonium hydroxide, rapid penetration occurs, as shown by an advancing front of the reagent. Copper absorption is highest at the surface as judged by the intense blue coloration, and progressive solution occurs, as shown in the series of photographs Fig. 5–8.

Filaments containing vinyl polymers, however, show various degrees of resistance to dissolution in cuprammonium hydroxide, depending in part on the polymer and its distribution in the filament. The high degree of swelling and the resistance to dissolution are well illustrated by monofilaments containing polyacrylonitrile. The extent of

swelling of a cross-section of a monofil (Sample No. 10) containing 10·3% of this polymer is shown in Fig. 9–12, the smooth contour throughout being characteristic of the swelling of viscose rayon containing polyacrylonitrile. After swelling had reached its limiting value, the section was disrupted mechanically and was shown to be gel-like, thus demonstrating that polyacrylonitrile had penetrated throughout the monofil structure.

Viscose rayon monofil (Sample No. 38) containing polymethacrylamide (45·7%) shows a somewhat similar resistance to dissolution (Fig. 13), which is rather surprising considering the water-sensitive nature of the polymer.

In contrast to acrylonitrile or methacrylamide, the less readily water-soluble monomers methyl methacrylate and styrene showed limited penetration of the viscose monofil structure, polymeric styrene being present only in a comparatively thin surface layer. When small lengths of viscose rayon monofil containing polystyrene were placed in cuprammonium hydroxide for 24 hr., the central portion dissolved, i.e. essentially that portion which remained unstained in the corresponding iodine staining experiment, and a hollow insoluble sheath was left. Similar shells were left after cuprammonium hydroxide had been applied to fibres containing polystyrene which had been extracted twice for an hour in boiling benzene. This behaviour is similar to that observed in a corresponding investigation on viscose rayon containing polymethyl methacrylate extracted successively with a vinyl polymer solvent and cuprammonium hydroxide. X-Ray examination of the residue showed that it contained both polymer and cellulose. The insolubility of the various residues suggests that, where polymer has been formed internally, an intimate mixture or combination of polymer and cellulose is obtained. Morton[3] also has commented on this aspect of polymer–fibre relationship with respect to polyacrylonitrile in viscose rayon.

3. STIFFNESS

The results of measurements of wet stiffness on rayon monofils containing various amounts of polymers are shown in Table I.

It is evident that in all cases the stiffness is increased by the deposition of polymer, the increase being substantial; in some cases the increase compares favourably with those brought about by treating viscose rayon with urea-formaldehyde resin or with formaldehyde in the presence of an acid catalyst. In general, the quantity of polymer rather than its nature appears to be the important factor in determining the wet stiffness of the treated monofil. This is illustrated in Fig. 14, in which the wet stiffness index is plotted against the amount of polymer deposited. It is interesting, however, to note that the curve representing the same relationships for monofils containing copolymer of styrene and acrylonitrile lies between the two curves obtained with the simple polymers. There is some evidence that the mode of depositing methyl methacrylate polymer does play some part in determining stiffness (cf.
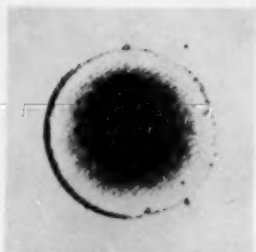
FIG. 1—Iodine Stain desorbing from Untreated Viscose Rayon. Stain eventually completely removed (× 50)
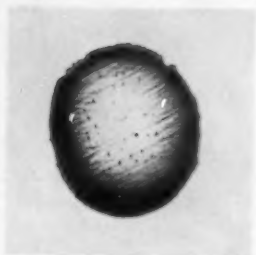
FIG. 2—Iodine Stain retained by Viscose Rayon containing Methyl Methacrylate Polymer (× 50)

FIG. 3—Iodine stains Loosely Adhering Surface Film when Preformed Polymer is applied from an Organic Solvent (× 50)

FIG. 4—Iodine Staining of Viscose Rayon Monofil containing Polystyrene (× 140)

FIG. 5
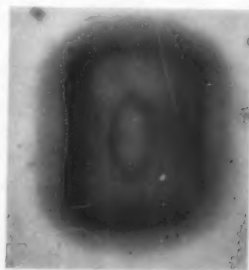
FIG. 6
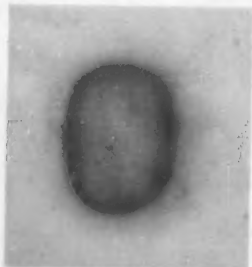
FIG. 7

FIG. 8

FIG. 5–8—Dissolution of a Short Length of Untreated Viscose Rayon in Cuprammonium Hydroxide (× 40)

FIG. 9

FIG. 10
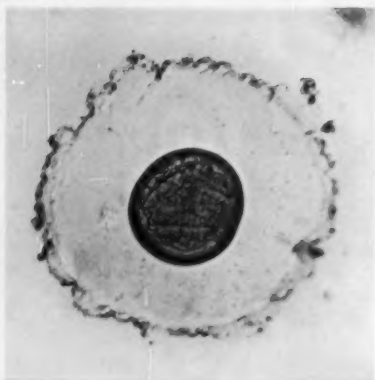
FIG. 11
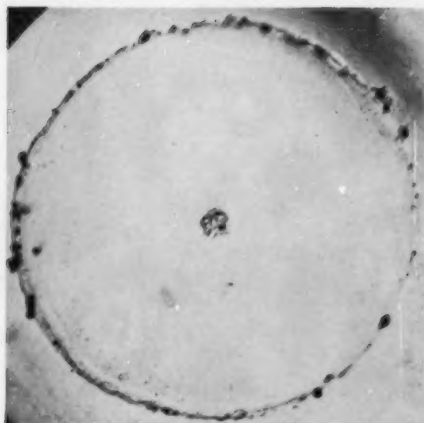
FIG. 12

FIG. 9–12— Progressive Swelling in Cuprammonium Hydroxide of Viscose Rayon containing Polyacrylonitrile: No Dissolution (× 53)
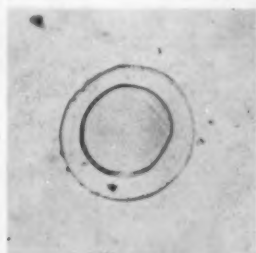
FIG. 13— Swelling in Cuprammonium
Hydroxide of Viscose Rayon con-
taining Polymethacrylamide: No
Dissolution (× 35)

the results for free-radical and thermal polymerisation methods in Table I).

TABLE I

Wet Stiffness of Viscose Rayon Monofil containing Vinyl Polymers

Polymer	Sample No.	Weight Increase (%)	Stiffness Index*
Untreated control	—	0	0.369 ± 0.006
Methyl methacrylate (thermal)	3	5.4	0.256 ± 0.005
	1	15.9	0.162 ± 0.006
	4	28.7	0.154 ± 0.007
	2	38.1	0.154 ± 0.006
Methyl methacrylate (free radical)	—	18.8	0.115 ± 0.002
	—	43.7	0.058 ± 0.002
Acrylonitrile ...	25	2.1	0.301 ± 0.008
	30	14.9	0.179 ± 0.010
	26	25.8	0.125 ± 0.007
	31	27.8	0.134 ± 0.003
	29	28.8	0.138 ± 0.008
	27	55.1	0.046 ± 0.004
	28	59.6	0.048 ± 0.002
Styrene	33	1.0	0.325 ± 0.013
	35	3.7	0.246 ± 0.010
	34	7.6	0.199 ± 0.010
	36	15.3	0.156 ± 0.009
	37	25.1	0.091 ± 0.006
Acrylonitrile– styrene	17	3.2	0.248 ± 0.007
	16	3.8	0.264 ± 0.007
	41	6.4	0.229 ± 0.008
	43	11.6	0.222 ± 0.019
	18	26.8	0.110 ± 0.005
	20	56.2	0.056 ± 0.003
	19	76.1	0.030 ± 0.002
	45	78.5	0.035 ± 0.002
Methacrylamide ...	40	1.4	0.368 ± 0.012
	39	2.7	0.353 ± 0.007
	38	45.7	0.126 ± 0.011

* Reduction in stiffness index corresponds to increased stiffness.

The increase in stiffness could arise from two causes— an increase in diameter due to polymer formation and a stiffening action caused by the rigidity of the polymer itself. The first is undoubtedly important, for, as is shown in the following section, there is a considerable increase in diameter resulting from the deposition of polymer. Regarding the second, it is interesting that the change in stiffness is not related simply to the physical properties of the polymer when not in association with a cellulose substrate. Thus, polyacrylonitrile deposited under the conditions used in this work is a friable solid; polymethacrylamide, while showing good film-forming properties, is highly water-sensitive; but polystyrene is water-insoluble and water-resistant.

4. CHANGES IN DIAMETER

The conditions for depositing polymer in the samples used for these experiments are given in Table II, which includes also values for the square of the diameter of the treated fibres measured at 65% R.H. and 22.2°c.
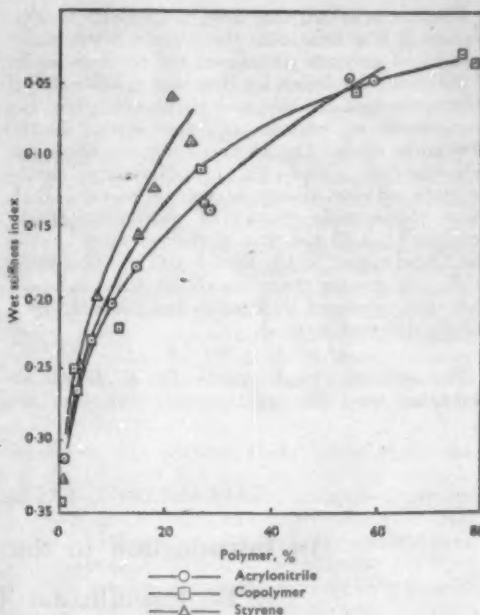
FIG. 14— Wet Stiffness of Viscose Rayon containing Various Polymers

TABLE II

Deposition of Methyl Methacrylate Polymer and Effect on Fibre Diameter*

H_2O_2 (%)	Temp. (°c.)	Weight Increase (%)	Increase in d^2† (%)
0.0003	25.0	14.3	9.6
0.0003	25.0	20.6	13.6
0.0006	25.0	27.7	20.9
0.0006	25.0	35.2	25.9
0.0009	32.5	51.2	34.3
0.0009	40.0	84.9	77.2
0.0009	40.0	98.8	89.5
0.0060	40.0	157.6	143.1
0.0060	40.0	176.2	167.8

* The concentration of ferrous ammonium sulphate was 0.1% and that of the monomer 4% in each case.

† d = Diameter of fibre.
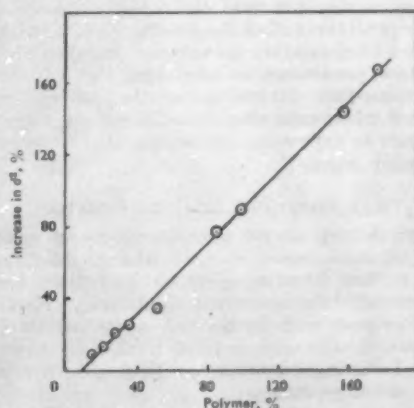
FIG. 15— Increase in Diameter of Viscose Rayon containing Methyl Methacrylate Polymer

These results are expressed graphically in Fig. 15, and it is evident that the relation between the amount of polymer introduced and the increase in d^2 is linear. As shown by Barr and Speakman [3], if length changes are assumed to be negligible, the data enable an estimate of "dead space" in the fibre to be made. Fig. 15 shows that the fibres can accommodate about 8% of polymethyl methacrylate without change in volume at 65% R.H. Since the specific gravity of polymethyl methacrylate [4] is 1·19 and that of viscose rayon [5] is 1·5, the "dead space" in the fibre is 10·1%. This value is slightly greater than, but of the same order as, that (6%) obtained by Preston and Nimkar [6] by a totally different method.

*   *   *

The authors wish to thank Dr. B. Booth for assistance with the experimental work, and the Directors of the Bradford Dyers' Association Ltd. for the award of a Research Fellowship to one of us (G.L.), which enabled the investigation to be carried out.

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EXPLANATORY PAPER ON MODERN THEORY

An Introduction to the Theory of Wool Dyeing

I—Equilibrium Theory of Affinity*

L. Peters

PREFACE

It is fairly widely felt that the present theory of wool dyeing is too complex and difficult to be understood by the practical dyer or the student beginner. This is mainly because of the thermodynamical and mathematical garb in which the theory has been presented hitherto, for in essence it is very simple (perhaps too simple), and can easily be understood by anyone with very little mathematical background.

Following the lucid and mainly qualitative description by Turner [1], the aim of the present paper is to explain in simple language the more quantitative aspects of the terms used and the concepts behind them. To succeed, some co-operation is required from the reader, as well as patience with the author for dealing, at first, with a number of elementary principles. Another prerequisite is persistence in continuing through the long intermediate discussion until the final section is reached, where some simple concepts are suggested which aim at expressing the essence of the theory in ordinary terms.

THE STRUCTURE OF WOOL KERATIN

Before delving deeply into the theory of wool dyeing, it is necessary to study the constitution of the protein (keratin) of which wool fibres are made, and its behaviour with simple acids. Keratin is a polymer made by Nature's secret process of condensing amino acids on to each other, as shown in the following equation, to form substituted amides called *peptides*—

$$NH_2 \cdot CH \cdot COOH + HNH \cdot CH \cdot COOH$$

Amino acids

$$\longrightarrow NH_2 \cdot CH \cdot CO \cdot NH \cdot CH \cdot COOH$$
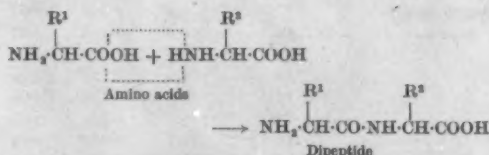
Dipeptide

These peptides are further condensed into long polypeptide chains, cross-linked by disulphide ($-S\cdot S-$) bonds in a sort of "vulcanisation" reaction called *keratinisation*, which makes the protein insoluble and probably flameproof too. This material is then "extruded", as wool fibres, from the growth cells (follicles) in the skin of the sheep. Their cellular form is rather complex but will not be described here, for it has been adequately expounded elsewhere [2].

The shape, the diameter, and the histological (cellular) structure of the fibres vitally affect the *rate* of dyeing, but when sufficient time has been allowed and the dye has finally penetrated all the accessible material, the *amount* then absorbed is determined only by the chemical constitution of keratin and the concentrations of dye and salts or acids in the external solution. Theories which deal with such equilibrium conditions may, therefore, justifiably ignore the physical structure of the wool fibre. Only later can we satisfactorily discuss the influence of the form of the fibres on the dyeing process.

Since keratin is made up of amino acids— the amino group of one condensed with the carboxyl group of another— each chain begins with a free carboxyl group and ends with a free amino group;

cyclic chains are excluded. Some of these amino acids (e.g. lysine and arginine) possess a second amino group, while others (e.g. glutamic and aspartic acids) possess an extra carboxyl group. In keratin, these extra amino and carboxyl groups are usually free at the end of side-chains, as shown in Fig. 1. It is these free groups which confer special dyeing properties on proteins such as wool, silk, casein, and Ardil fibres, properties which differentiate them markedly from cellulosic and other fibres.

B — Side-chain of amino-acid residue
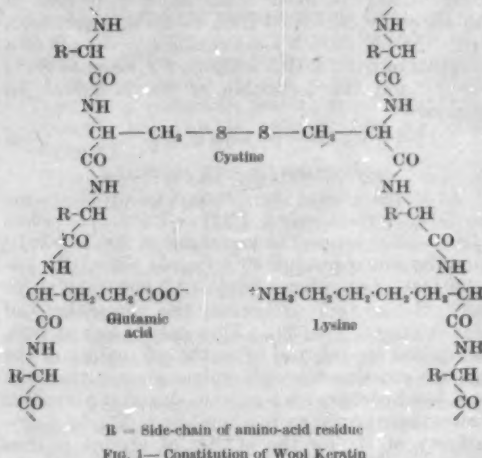
FIG. 1— Constitution of Wool Keratin

To simplify the picture, then, keratin can be represented as a vast insoluble polybasic amino acid having the formula—

$$(NH_2)_mB(COOH)_n$$
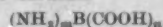
where B represents the unreactive residues of the amino acids and the main-chain peptide backbone—

the Rs representing the side-chains.
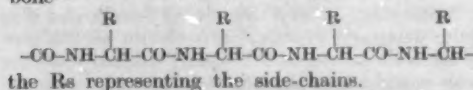
TITRATION OF AMINO ACIDS

Let us first consider the behaviour of a simple soluble amino acid, for it is easy to see that a large polymeric amino acid like keratin will behave in a somewhat similar way, and the extra effects of its polybasic properties and insolubility can be taken into account later. The simplest amino acid is glycine ($NH_2 \cdot CH_2 \cdot COOH$, aminoacetic acid); when it is dissolved in water, the acidic carboxyl group –COOH permits its hydrogen to break away (because –COO⁻ has little affinity for H⁺), but the amino group promptly snaps it up (since –NH₂ has a high affinity for H⁺). The –COOH becomes –COO⁻ and the –NH₂ becomes –NH₃⁺, each glycine molecule then having the structure—

$$^{+}NH_3 \cdot CH_2 \cdot COO^{-}$$

which is called a *zwitterion** or "hybrid ion", since it is neither a cation nor an anion but has both positive and negative charges. Naturally, the

* *Zwitter* (German) = "dual", from *zwei* = "two".

negatively charged –COO⁻ group of one molecule can attract the positively charged –NH₃⁺ group of another to form a *salt-link*, but this is only temporary if the solution is dilute, since bombardment by other molecules (thermal agitation) tends to break up any such association.

When acid (e.g. hydrochloric acid) is added to the solution, the increased concentration of hydrogen ions in solution forces some of them back on to the –COO⁻ to re-form –COOH. When the concentration of the acid is approx. 0·005 N., 50% of the carboxyl groups present, on the average, are thus "back-titrated". No matter how much acid is added, however, it is not possible to reconvert all the carboxyl ions to –COOH: a small proportion must always remain, although it may be extremely minute. For instance, when the acid is 0·05 N. only 9% remain; in 0·5 N. acid the proportion is less than 1%.

The positively charged –NH₃⁺ group repels the similarly charged H⁺ but attracts the chloride anion and, if the solution were evaporated, glycine hydrochloride Cl(NH₃·CH₂·COOH) would crystallise out. This compound is obviously a substituted ammonium chloride and, if the chloride ion were coloured, it would not appear entirely ridiculous to say that the coloured crystals were "dyed" glycine. In fact, dye acids do form such coloured crystals with amino acids. But as soon as the hydrochloride is redissolved in water, the chloride ion leaves its positively charged partner in the same way as it would in ordinary ammonium chloride. This is because, in water, Cl⁻ has very little affinity for –NH₃⁺. In a similar way, dyes which are not fast to washing have very little affinity for the material and leave it by going back into solution.

MODERN IDEAS OF ACIDS AND BASES

From the above, it appears that glycine combines with acid through its –COO⁻ groups. According to the modern theory of acids and bases, which defines a base as an atom, ion, or group of atoms which can combine with hydrogen ions, the –COO⁻ group must be a basic group. To call a –COO⁻ group "basic" seems at first sight contrary to all one's usual ideas; but if it is remembered that –COOH is still regarded (on this theory) as an acid because it can give off H⁺, there will be little difficulty in getting used to this way of looking at things. Besides, the fact that a solution of sodium acetate in water is definitely alkaline shows that CH₃·COO⁻ is actually basic.

If alkali (caustic soda, say) is added to a solution of glycine, the hydroxyl ions from the sodium hydroxide at first mop up any free H⁺ in the solution and form H₂O; but, as the alkali concentration increases, the OH⁻ ions begin to compete with –NH₂ for possession of the available H⁺. When the alkali concentration is approx. 0·00005 N. about 50% of the –NH₃⁺ groups lose their hydrogen ions and revert to –NH₂ groups; at 0·0005 N. only 9% are still –NH₃⁺; while at 0·005 N. the amount falls to less than 1%. From this we see that the alkali-combining capacity of glycine is determined by the number of –NH₃⁺ groups, and these must,

therefore, be regarded as *acidic*. Again there is nothing but unfamiliarity against this viewpoint, for an acid, by definition, is an atomic group or ion which can give off hydrogen ions. Solutions of ammonium chloride are thus distinctly acid in taste, because the NH_4^+ ions give off H^+. Uncharged $-NH_2$ groups, however, must still be considered basic, for they can combine with acid, i.e. with H^+.

AFFINITY FOR HYDROGEN IONS

All these facts show that $-COO^-$ has little affinity for H^+, $-NH_2$ has a greater affinity, and OH^- has the greatest affinity. H^+ and $-NH_3^+$ have very little affinity for Cl^- in aqueous solution, since both HCl and $-NH_3Cl$ then break down completely into separate ions. Here we are confronted with the property of relative affinity, which is going to play such an important part in the later discussion and which should, therefore, be thoroughly understood in this simple case, before we proceed to the more complicated problem of the affinity of wool for dye acids.

The best way of comparing the affinity of these groups for H^+ is to compare the concentration of acid, or more strictly that of hydrogen ions, necessary to keep the group 50% ionised. To do this for the amino group, however, we need to know the value of the hydrogen ion concentration in alkaline solutions, and we can find this only by considering a special property of water.

It has been found from conductivity measurements that, in aqueous solutions, when the concentration of hydrogen ions ($[H^+]$ moles/litre) is high, the concentration of hydroxyl ions ($[OH^-]$ moles/litre) is low; and, *vice versa*, when $[H^+]$ is low, $[OH^-]$ is high. When the two concentrations are multiplied together, they always give the same value (the *ionic product*, which is related to the dissociation constant of water) at any given temperature. Thus at 25°c.—

$$[H^+] \times [OH^-] = \frac{1}{100,000,000,000,000} \qquad (i)$$

In 0·001N-NaOH the hydroxyl ion concentration is 1/1000, and so $[H^+]$ must be 1/100,000,000,000. It becomes tiresome to have to write so many zeros, and the above fraction is usually abbreviated to $1/10^{11}$ or 10^{-11}, the superscript showing the number of zeros when it is written out in full. With this notation, equation (i) is more simply written as—

$$[H^+] \times [OH^-] = \frac{1}{10^{14}} = 10^{-14} \qquad (ii)$$

THE pH SCALE

The superscript number is called an index, exponent, logarithm, or *power*, and since it is the important part of the number, a further abbreviation can be used, in which a solution having a hydrogen ion concentration of $1/10^{11}$ (as in the above 0·001 N-NaOH solution) is said to have a pH of 11, where "p" can be thought to stand for the "power" of the hydrogen ion concentration. Similarly, in 0·01 N-HCl, where $[H^+] = 1/100$ or $1/10^2$, one says that the solution has a pH of 2.

In pure water to which no acid or alkali has been added, $[H^+] = [OH^-]$, and for the product of the two to equal $1/10^{14}$ (according to equation (ii)), each must be $1/10^7$; pure water at room temperature, therefore, has a pH of 7*. Alkaline solutions at room temperature thus have pH values greater than 7, and acid solutions have pH values less than 7. On this scale, 10 N-HCl has a pH of approx. —1, and 10 N-NaOH has a pH of 15— the most extreme values ever likely to be encountered in practice. The pH values for concentrations intermediate between whole-number powers of 10 are easily calculated from tables of logarithms, since the pH scale is logarithmic; e.g. the pH of a solution of 0·002 N-HCl is about 2·7, because $[H^+] = \frac{1}{500}$ and the logarithm of 500 is 2·699. In general—

$$pH = \log \text{ (litres per mole of } H^+) \qquad (iii)$$

AFFINITIES ON THE pH SCALE

As stated above, the carboxyl group of glycine is 50% ionised when $[H^+] = 1/200$, i.e. when pH = 2·3 (because the logarithm of 200 is 2·301); and the amino group is 50% ionised when $[OH^-] = 1/20,000$, i.e. when $[H^+] = 1/5,000,000,000$ or at pH = 9·7 (because the logarithm of 5,000,000,000 is 9·699). These pH values at 50% ionisation are referred to as the pK values of the groups concerned; at pH values greater than the pK, less hydrogen ion is combined; and at pH values lower than the pK, more is combined. The fairly low affinity of H^+ for the $-COO^-$ of glycine is thus represented by the low pK value of 2·3, and the high affinity between H^+ and the $-NH_2$ of glycine is measured by the high pK value of 9·7. In acid dyeing, we are concerned with the affinity of dye *anions* rather than hydrogen ions, but it will illuminate the later discussion if we study in more detail the affinities of H^+ for basic groups.

THE DILUTION SCALE OF AFFINITIES

Affinity can be measured on any scale, and it is quite arbitrary what value is chosen as the zero of the scale so long as it is clearly realised what the scale is and where the zero is taken to be. On the pH scale of affinities, a group is implicitly assumed to have zero affinity if it is only 50% ionised at pH = 0, i.e. in N-HCl. Unit affinity of H^+ for a group on this scale is based on taking a dilution of 10 : 1 as a unit, because when a normal solution of hydrochloric acid is diluted to ten times its volume with water, its pH changes from 0 to 1. Diluting this, in turn, ten times changes the pH from 1 to 2; and so on. The acid now occupies a larger volume, in the same way as a gas does when it is allowed to expand. To compress such an expanded gas back to its original volume, a certain amount of mechanical work has to be done; in a similar fashion, to concentrate the diluted acid back to its original strength also involves the expenditure of the same amount of work or energy. By setting up a special electrical apparatus, this energy of dilution or concentration can be accurately measured as a potential difference— so many volts— which can be expressed in the same pH units as above.

* At 100°c. $[H^+] \times [OH^-] = 1/1,800,000,000,000 = 1/10^{12\cdot25}$, so the pH of pure water at the boil is 6·13.

Such a device is a potentiometer, but when used to measure hydrogen ion concentrations it is called a *pH-meter*. These instruments have, by now, become standard pieces of laboratory equipment, and they now play the same part as the dyer's tongue did in the past when he used it to taste the dye liquor to see whether the dyebath was sour enough, i.e. sufficiently acid.

THERMODYNAMIC SCALE OF AFFINITIES

The work required to compress a perfect gas to one-tenth of its volume has been found to be about 1·36 kilocalories per gram-molecule (kcal./mole) at 25°c. By analogy, this is taken to be the work or energy needed to concentrate a solution containing one mole of solute to ten times its strength. (There is a correction factor, the "activity coefficient", but this is approx. 1·00 for dilute solutions.)

This energy of concentration (at 25°c., say) can thus be directly calculated from a pH value by multiplying it by 1·36 kcal./mole*. The affinity of H+ for the carboxyl group in glycine, expressed in these other units, is thus $2 \cdot 3 \times 1 \cdot 36 = 3 \cdot 13$ kcal./mole, while its affinity for the amino group is, similarly, $9 \cdot 7 \times 1 \cdot 36 = 13 \cdot 19$ kcal./mole. These values can be looked upon as indicating the degree of attraction for H+ of the two groups, in that they represent the work required to tear away 1 mole of H+ from each group when it is half-saturated. This is the thermodynamic scale of affinities.

The concentration of H+ at which the group is able to hold on to half the possible maximum is chosen because it is the simplest to measure. Any other fraction could, conceivably, be selected, except that of the fully ionised or fully unionised form. In the case of –COO–, for instance, to force all of them to become –COOH would require an enormous concentration of H+— even in 10N-HCl part (1/1000) would still be ionised; while to ionise this group completely the solution would have to be extremely alkaline, although at pH 7 there would only be 1/100,000 unionised.

It is also easy to calculate the position of the midpoint when the hydrogen ion concentration at any other point is known. All that need be done is to multiply the actual concentration by the proportion of groups uncombined and divide by the proportion of groups combined. For example, suppose that the groups are 40% combined when [H+] = 1/150, i.e. 2 out of every 5 carboxyl groups are combined and 3 are uncombined, so that it will be half ionised at a higher concentration—when $[\text{H}^+] = \frac{2}{3} \times \frac{1}{150} = \frac{1}{100}$, i.e. at pH = 2. If it is $\frac{5}{8}$ combined when $[\text{H}^+] = \frac{1}{50}$, 5 out of every 8 groups are combined and 3 are uncombined, and it will be half ionised at a lower concentration, viz. when $[\text{H}^+] = \frac{3}{5} \times \frac{1}{60} = \frac{1}{100}$ as before. This rule can be expressed in a formula—

$$K = [\text{H}^+]_{\frac{1}{2}} = [\text{H}^+] \times \frac{[\text{Uncombined}]}{[\text{Combined}]} \qquad \text{(iv)}$$

where [H+]½ is the hydrogen ion concentration at 50% combination and [H+] is that at some other

* 1360 = 2·303 *RT*, since *R* is 2 cal./mole per °c. and *T* is the absolute temperature (*t*°c. + 273).

A4

degree of combination. If this formula is written logarithmically, the pK can be calculated from the equation—

$$\text{p}K = \text{pH} - \log \frac{[\text{Uncombined}]}{[\text{Combined}]} \qquad \text{(v)}$$

TITRATION OF WOOL KERATIN

When wool combines with acid or alkali, its free carboxyl groups (but not the amino groups) behave very similarly to those of glycine. At pH values below 1·0 wool appears to be completely saturated with acid, the amount being about 80 gram-equivalents per 100 kilograms of dry wool. At pH 2·2 wool has combined with 40 g.-equiv. per 100 kg.— about half as much acid as it can ultimately take up— but not until pH 13 is reached does it combine with an equal amount of alkali.

Although the hydrion-combining curves for wool and glycine are so similar, the anion-combining curves are very different. As has been pointed out above, the –NH₃+ groups of glycine have hardly any affinity for Cl–, and in solution there is no formation of a compound like –NH₃Cl. Yet when wool combines with HCl, it takes out of solution just as many chloride ions as it does hydrogen ions. This seems strange, because the amino groups in wool are the same as in glycine, but the above fact makes their affinity for chloride ions appear to be different. Since the dyeing of wool with acid dyes is essentially one of absorption of coloured anions, it is of great importance to establish the cause of this difference. However, calculation shows that the fibres would acquire an electric potential of several million volts if they combined only with H+ ions, and it would then be impossible to pull the wool out of the solution without as many chloride ions leaving the solution because of the enormous electrical attraction. Most of the affinity of wool for chloride ions and acid dye anions is thus due to wool being able to combine with hydrogen ions and so become positively charged.

The positively charged groups are attached to the protein structure and are not free to diffuse back into the solution, but the chloride ions are not so attached and can return to the outer solution. Long ago, the famous American chemist, Willard Gibbs, laid down the laws which must be obeyed in such a system, and later F. G. Donnan used them to show that an unequal distribution of non-diffusible charged groups would force the diffusible ions also to be distributed unequally. He showed that, however unequal the division may be, the value obtained by multiplying together the concentrations of H+ and Cl– in a solution must be equal to that obtained by multiplying the concentrations of diffusible H+ and Cl– of any other system in equilibrium with the solution. This holds also for any pair of oppositely charged diffusible ions. Peters and Speakman [3] applied this law— the so-called *Donnan membrane equilibrium law*— to experimental data on the combination of wool with hydrochloric and sulphuric acids in presence of salts. They had to assume that the acid-swollen fibres contained an internal free

volume (about 35 litres per 100 kg. of wool) in which were dissolved the chloride and free hydrogen ions in equilibrium with the external solution. Then the Donnan law leads to the equation—

$$[H^+]_{ext} \times [Cl^-]_{ext} = [H^+]_{int} \times \frac{[Combined\ acid]}{Internal\ volume} \qquad (vi)$$

since all the "combined" chloride is assumed to be free to move about in the internal volume (the suffixes "ext" and "int" refer to the external and internal solutions respectively).

Because the internal volume (in litres per 100 kg.) has nearly the same numerical value as half the maximum acid-combining capacity (in equivalents per 100 kg.) the previous equation can be approximately written as—

$$[H^+]_{ext} \times [Cl^-]_{ext} = [H^+]_{int} = K_{int} \qquad (vii)$$

when these refer to the standard state chosen.

The affinity of wool for hydrochloric acid is proportional to $[H^+]_{int}$ and thus cannot be calculated from $[H^+]_{ext}$ alone but must include $[Cl^-]$ as well. Putting equation (vii) in logarithmic form gives—

$$pK_{int} = pH_{ext} - \log [Cl^-]_{ext} \qquad (viii)$$

But the Donnan theory is not the only one that has been put forward to explain the combination of wool with acids. Because of its simplicity and ease of application, that of Gilbert and Rideal[4] has become very popular. This theory assumes that even chloride ions have some affinity (though small) for the charged amino groups, and on this basis Gilbert and Rideal derived the equations for the combination of acids when the anions as well as the hydrions are adsorbed at certain sites. They assumed also that all the –COO⁻ groups have the same affinity for H⁺ and that in wool there are an equal number of –NH₃⁺ groups all having the same affinity for anions. The first assumption may not be greatly in error, for the acid-combination curve looks much like the titration curve of a simple monobasic carboxylic acid. But the second assumptions may be wrong, because the alkaline titration curve of wool is different from the acid one and the amino groups in wool are known to belong to different chemical structures, e.g. –NH₂ from lysine, –NH·C(NH₂):NH from arginine,
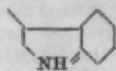
[structure] from tryptophan, and [structure]

from histidine side-chains. Nevertheless, they are simplifying assumptions and, as far as simple anions are concerned, all the positively charged nitrogen atoms in each group may be regarded as similar.

With these assumptions, Gilbert and Rideal were able to write equations of the same form as (iv) for anions as well as for hydrogen ions—

$$K_H = [H^+] \times \frac{[Uncombined\ sites]}{[Combined\ hydrions]} \qquad (ix)$$

$$K_{Cl} = [Cl^-] \times \frac{[Uncombined\ sites]}{[Combined\ anions]} \qquad (x)$$

By multiplying these two together, one obtains the Gilbert–Rideal equation in the simple form—

$$K_{HCl} = [H^+] \times [Cl^-] \times \frac{[Uncombined\ sites]^2}{[Combined\ acid]^2} \qquad (xi)$$

since combined acid is equivalent to combined H⁺ or Cl⁻ because of the above-mentioned enormous electrical potential.

The constant $K_{HCl} = K_H \times K_{Cl}$ is a measure of the affinity of wool keratin for both hydrogen ions and chloride ions.

Choosing the point where the proportion of combined acid equals the proportion of uncombined sites, i.e. at half-saturation—

$$K_{HCl} = [H^+]_{\frac{1}{2}} \times [Cl^-]_{\frac{1}{2}} \qquad (xii)$$

and putting this in the logarithmic form gives—

$$pK_{HCl} = pK_{ext} - \log [Cl^-]_{ext} \qquad (xiii)$$

just as in the Donnan theory. According to both the Gilbert–Rideal and Donnan theories, therefore, the true pK of wool for HCl is twice the external apparent pK in the absence of salt, for then—

$$pH = - \log [Cl^-] \qquad (xiv)$$

since $[H^+] = [Cl^-]$ when only hydrochloric acid is present.

The difference between the two theories concerns the value to be assigned to the internal volume. Peters and Speakman[3] assume that it is the amount by which the fibres swell in going from the dry state to equilibrium in the acid solution. With anions having less affinity than H⁺, the fibre will have a positive charge, and free anions will be attracted into the internal solution over and above those actually adsorbed at sites. The Gilbert–Rideal theory, however, assumes that the amount of such "combined" but unadsorbed anions is negligible, which would be true only if the internal volume were very small. With a minute internal volume, the concentration of free anions becomes large enough to compel all the anions, in spite of their low affinity, to go on to the sites, as they would in a hydrochloride in the solid state.

The two theories are thus similar in that they both say that the amount of acid adsorbed should be proportional to the product of the concentrations of hydrogen and chloride ions, but they differ in the value each assigns to the internal volume. The Gilbert–Rideal theory assumes that both ions are adsorbed at definite sites and also postulates that the form of the adsorption equation is that given by (xi), which is the Langmuir adsorption equation. The Donnan treatment of Peters and Speakman, however, does not need this last postulate, but leaves open the question of the form of the internal adsorption equation. They showed that there was a unique internal titration curve, but did not derive an equation to fit it.

Fortunately, it is possible to ignore the above differences between these two theories and to apply that part of dyeing theory which is common to both. The pH at the point where 40 gram-equivalents of acid combine with 100 kg. of wool (the pK) is a measure of the affinity on either theory, and both require it to be doubled, when

salt is absent, to take account of both ions. In the presence of the salt of the acid, both agree that the affinity of wool for the acid $(-\Delta\mu)$* is approximately proportional to $pK - \log(\text{anion concn.})$. The symbol $-\Delta\mu$ represents the change in free energy which one gram-molecule of the acid undergoes in being absorbed, the negative sign showing that it *loses* energy, as if going on to the wool were the same as falling to a lower energy level. The further it falls, the harder it must be to get off again, and this is in agreement with the usual idea of affinity.

Dye acids are sulphonic acids and combine with wool in much the same way as does hydrochloric acid, so they can be treated in the same way. It is by using similar equations that the values quoted in the literature for the affinities of acid dyes have been calculated (see examples below). So long as the dyes are monobasic, the equations derived for hydrochloric acid can be applied, but if they are polybasic the equations are relatively easily altered to take this into account. Nevertheless, for the sake of simplicity in the following treatment only the case of monobasic acid dyes will be considered.

FASTNESS TO WASHING

One of the practical tests for high affinity in a dye is its fastness to washing. The thermodynamic method of expressing the affinity of dyes for wool is essentially the same, expressed more precisely but dressed up in a less obvious way. The affinity, as pointed out before, is the free energy of the solution of the dye acid which is in equilibrium with wool dyed to 50% saturation. The free energy (at 100°c.) is given by—

$$-\Delta\mu = 1\cdot7\,[pK - \log(\text{anion concn.})] \qquad (xv)$$

which means that a high affinity corresponds to a high pK value at a small anion concentration. It is not the *concentration*, therefore, which measures affinity, but the *dilution*. In other words, the affinity is not measured by how many moles of dye per litre are left in solution when the wool has become 50% saturated but by the number of litres per mole needed to reach the same state. Imagine an amount of wool sufficient to combine with 2 moles of dye (about 2 kg. of wool would do), dyed to saturation in the free dye acid alone and then soaked in enough water to allow 1 mole of dye to bleed off again by the time equilibrium is reached. Then the volume of water required is a measure of the affinity of that dye acid: a small volume means a low affinity, and a large volume means a high affinity. We can take a dye as having zero affinity when only 1 litre is required to strip off half the dye from the above amount of fully saturated wool, and we can choose 10 litres as a unit of affinity, 100 litres as 2 units, 1000 litres as 3 units of fastness, and so on (i.e. we can use a logarithmic scale). This scale is, in effect, the modern thermodynamic method of measuring affinity. The only difference is that a fastness at

* Pronounced "delta mew". Δ is the Greek letter "D" and stands for "difference"; the difference is between the energy level of the dye solution at equilibrium and that of a normal solution, viz. of concentration 1 g.-equiv./litre. μ is the Greek letter "m" and stands for "molar"— the molar free energy or free energy per mole.

100°c. corresponding to 10 litres/mole is expressed on the thermodynamic scale as an affinity of 3·4 kcal./mole, 100 litres/mole as 6·8 kcal./mole, 1000 litres/mole as 10·2 kcal./mole, and so on: 3·4 kcal./mole for each tenfold dilution*. Intermediate dilutions are expressed by using the logarithm of the dilution. For example: a fastness of 500 litres/mole corresponds to an affinity of $2\cdot699 \times 3\cdot4 = 9\cdot2$ kcal./mole, because the logarithm of 500 is 2·699.

In this way, it is possible to correlate in one's mind the published values for the affinities of dyes with the ordinary concept of fastness to washing (see Fig. 2).

DEGREE OF EXHAUSTION

The other practical way of expressing affinity is to quote the final "degree of exhaustion" of a dyebath of specified initial concentration, acidity, and liquor/wool ratio. It is related to the thermodynamic affinity, but must depend also on the ratio of liquor to wool, because if very little wool is present the bath cannot be fully exhausted even when the affinity is high; but if there is a large excess of wool, a dye of quite low affinity might be able to exhaust completely. Although the result can be affected by the acidity of the solution, it is independent of the depth of dyeing provided that the latter is small (~1% on the weight of the wool) and the molecular weight of the dye is large (~300). Fig. 2 shows how the observed "degree of exhaustion" under such conditions depends on the value of the affinity when the liquor/wool ratios are 10, 30, and 50 : 1 in 0·01 N-HCl at 100°c. (the solution is assumed to be at pH 2·15 and the wool to be 50% saturated with dye acid and HCl).

From this it can be seen that dyes with affinities larger than 7–9 kcal./mole exhaust from the dyebath satisfactorily, i.e. with better than 90% exhaustion.

NUMERICAL EXAMPLES

EXAMPLE 1— What is the thermodynamic affinity of hydrochloric acid for wool at 100°c., given that the pH of half saturation is 2·15?

In the absence of salt, the hydrogen ion and chloride ion concentrations are equal. The pK for HCl is thus twice the pH value, i.e. $pK_{HCl} = 4\cdot30$. Its thermodynamic affinity $-\Delta\mu = 4\cdot30 \times 1\cdot7 = 7\cdot31$ kcal./mole.

EXAMPLE 2— If the free acid of Orange II is able to half-saturate wool at 100°c. when the pH is 3·66, what is its affinity?

Thermodynamically, it is $2 \times 3\cdot66 \times 1\cdot7 = 12\cdot24$ kcal./mole. On the fastness-to-washing scale it is 4600 litres/mole, since antilog 3·66 = 4600.

EXAMPLE 3— A monobasic sulphonic acid dye of molecular weight 250 gives a 1% dyeing with the free dye acid alone, the final pH of the dyebath being 4·0. How would one calculate from these data the affinity of the dye and the degree of exhaustion?

For a 1% dyeing, there will be 1000 g. of dye on 100 kg. of wool, i.e. $1000/250 = 4$ g.-equiv. of dye. We know that 100 kg. of wool can take up as much as 80 g.-equiv. of dye, so there must be room

* 3400 = $2 \times 2\cdot303\,RT$ as above (see p. 177), the difference being due to the higher temperature.

for another 76. The hydrogen ion concentration is, according to the pH value, $1/10^4 = 0.0001$ mole/litre when only 4 g.-equiv. are combined; but to get 40 g.-equiv. to go on to the wool, i.e. to get 50% saturation, the solution would have to be more acid— a higher hydrogen ion concentration— in fact 76/4 = 19 times as big. The concentration of dye acid would then be 19/10,000 mole/litre, and the affinity therefore 10,000/19 = 526 litres/mole. But since $pK = \log 526 = 2.72$, the thermodynamic affinity $-\Delta\mu = 2 \times 2.72 \times 1.7 = 8.25$ kcal./mole.

It is quicker, however, to carry out the calculation directly on the logarithmic scale as follows: Only if the pH is lower than 4.0 (corresponding to a more acid solution) will 100 kg. of wool combine with 40 g.-equiv. of dye, i.e. at a pH of $4.0 - \log 19 = 4.0 - 1.28 = 2.72$, and the affinity is $2 \times 2.72 \times 1.7 = 8.25$ kcal./mole as before.

In general, the affinity at 100°c. (in kcal./mole) is given by the equation—

$$- \Delta\mu = 3.4 \left(\text{pH} - \log \frac{[\text{Uncombined}]}{[\text{Combined}]} \right)$$

The degree of exhaustion, however, can be calculated only if the ratio of dye liquor to wool is known. Let us suppose it to be 50 : 1 in this example, so that there is 5000 litres of liquor per 100 kg. of wool. Since no other acid is present, the dye remaining in solution at pH = 4.0 is, by definition, 1 g.-equiv. in $10^4 = 10,000$ litres; 5000 litres, therefore, contains 0.5 g.-equiv. of dye acid. From the above data, we know that 4 g.-equiv. have gone on to the wool, so there must have been a total of 4.5 g.-equiv. of dye added initially. The exhaustion is thus 4.0/4.5 = 89%.

EXAMPLE 4— Suppose a monosulphonic dye of molecular weight 500 gives a 1% dyeing in a solution of hydrochloric acid at 100°c. if the pH is 2.15. What is the affinity of the dye if its exhaustion is 80% when the liquor : wool ratio is 50 : 1?

From the figure of 1% dye on the weight of the wool, it follows that 1000/500 = 2 g.-equiv. of dye anion are combined per 100 kg. of wool. But we know from Example 1 that wool will be half-saturated with H+ at pH 2.15 under these conditions, and the 40 g.-equiv. of H+ must be balanced by an equal number of anions. There must, therefore, be 38 g.-equiv. of chloride ion combined. The affinity of the dye anion (in litres/mole) would appear to be $\frac{2}{38} = \frac{1}{19}$ of that of chloride if the ratio of the amounts combined were the only consideration, but one must also allow for the relative concentrations of dye and chloride ion present in the dyebath. From the value of 80% exhaustion, the ratio of dye in solution to that on the fibre must be 20 : 80, so $\frac{20}{80} \times 2 = 0.5$ g.-equiv. of dye per 100 kg. of wool is left in solution, the volume of which is 5000 litres. The dye concentration in solution is thus 0.5/5000 = N./10,000, but the chloride concentration is approx. N./143, since antilog 2.15 = 143. The dye affinity (as a fastness-to-washing figure) is thus 10,000/143 times as big as would appear from the relative amounts of dye and chloride absorbed.

Since the pK of HCl is 4.30, that of the above dye is—

$$4.30 + \log \left(\frac{10,000}{143} \times \frac{1}{19} \right) = 4.30 + 0.57 = 4.87$$

from which $-\Delta\mu = 1.7 \times 4.87 = 8.28$ kcal./mole.

In general, the pK of a dye acid is related to the pK of the acid in which dyeing takes place by a formula of the form—

$$pK_{HD} = pK_{HCl} + \log \left(\frac{\text{Chloride in soln. in moles/litre}}{\text{Chloride combined in moles/100 g.}} \right)$$

$$+ \log (\text{liquor/wool ratio}) - \log \left(\frac{100 - E}{E} \right) + 3.08 \ *$$

or

$$- \Delta\mu = - \Delta\mu_0 - 1.70 \log \left(\frac{100 - E}{E} \right)$$

where E is the percentage exhaustion and $-\Delta\mu_0$ is the affinity which would give 50% exhaustion at the given liquor ratio. It was from such an equation that the curves of Fig. 2 were constructed.

Liquor Ratio	Standard Affinity $-\Delta\mu_0$ kcal./mole
50 : 1	7.15
30 : 1	6.78
10 : 1	5.96
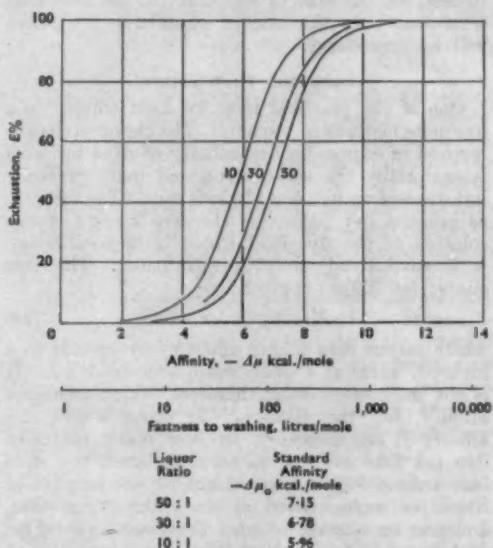
FIG. 2— Dyeing from Hydrochloric Acid at 100°c., pH = 2.15, for Very Small Percentage Dyeings

References

[1] Turner, J.S.D.C., **71**, 29 (Jan.), 96 (Feb. 1955).

[2] *Wool Science Review*, **1**, 3 (1948).

[3] Peters and Speakman, J.S.D.C., **65**, 63 (1949).

[4] Gilbert and Rideal, *Proc. Roy. Soc.*, **A 182**, 335 (1944); Gilbert, *ibid.*, **A 183**, 167 (1944).

Suggested Reading

Vickerstaff, T., *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 2nd edition 1954).

Bird, C. L., *The Theory and Practice of Wool Dyeing* (Bradford: Society of Dyers and Colourists. 2nd edition 1951).

*3.08 = log 1250, the equiv. wt. of keratin being taken as 1250.

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Explanatory Papers on Modern Theory

As a very ordinary member of the Society, I want to express my opinions on the *Journal*.

On page 29 of the January 1955 issue there is a foreword signed by John Barritt, Chairman of the Publications Committee, which contains some sound common sense.

Then follows the paper by H. A. Turner—a most excellent paper on a most difficult subject. It looks as though someone has at last seen the light! For years, many of the publications in the *Journal* must have appealed to a very small proportion of its readers.

In my opinion, the Society should follow the example of some other learned societies, e.g. the Royal Horticultural Society, who have *two* journals— one for those who *grow* plants (the practical dyers) and one for those who are mainly interested in what makes them "tick", i.e. the backroom types. It will be said that the two merge: they do, but most people have a limited amount of grey matter and time, and cannot follow both types of journal in real life.

I suggest that the Publications Committee consider having two journals—

   I— A monthly carrying all the advertisements, news, papers of the H. A. Turner type, and *appropriate* abstracts.

   II— A quarterly journal carrying the "backroom" papers with appropriate abstracts and advertisements.

The quarterly to be available to members by request only, perhaps even at an extra charge.

<div align="right">D. S. O'BRIEN</div>

13 CAMBORNE WAY
   HESTON
     MIDDLESEX

31st January 1955

I would like to comment on the most aptly worded Foreword by Mr. John Barritt on p. 29 and on the excellent article by Mr. H. A. Turner which follows immediately afterwards. Many of our clients, almost without exception members of the Society, have over a considerable period expressed the need for such a course of action as a deeply felt want; some of the more expressive have implied that Mr. Barritt's third sentence might in justice be re-worded to read: "It is certain, however, that everyone concerned with the *theory* of dyeing would benefit by an understanding of modern *practice*"!

<div align="right">D. HOLGATE
for ANALTEX</div>

BAILDON
   SHIPLEY
     YORKSHIRE

31st January 1955

Turner's successful attempt [1] to explain current theories of dyeing is a very welcome contribution to our subject. As no doubt it will be read by many, it is of importance that any inaccuracies be challenged.

Turner states (p. 38) that in direct cotton dyes "hydrogen-bond-forming groups must be spaced along the length of the molecule so that certain pairs of them are exactly, or very nearly, the same distance apart as some of the hydroxyl groups which are regularly spaced along the length of the cellulose molecule". This admittedly attractive idea was first publicly stated, I believe, by Vickerstaff [2], and has since been quoted repeatedly.

However, Robinson [3] has shown, using his molecular models, that the surface of the cellulose chain is such that hydrogen bonding by means of one or other hydroxyl group can occur at any position along its length, and that therefore the repeat of 10.3 A. is unlikely to be of importance in this respect. Further, many direct cotton dyes do not contain groups capable of hydrogen bonding at a distance apart of $10–11$ A. (or a multiple thereof) [4,5].

Thus Turner's statement and similar ones made by others are not founded on fact.

Naturally, this point has no bearing on the question of whether hydrogen bonding does or does not take place between dye and cellulose during the process of dyeing, but relates only to the structural features which a dye must possess before it will exhibit substantivity.

<div align="right">HARRY E. NURSTEN</div>

DEPARTMENT OF LEATHER INDUSTRIES
   THE UNIVERSITY
     LEEDS 2

27th January 1955

References

[1] Turner, J.S.D.C., 71, 29 (Jan. 1955).
[2] Vickerstaff, *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 1950).
[3] Robinson, *Discussions Faraday Soc.*, (16), 125 (1954).
[4] Zollinger, *ibid.*, p. 123.
[5] Nursten, *ibid.*, p. 231.

I am sure that Mr. Barritt, the Publications Committee, and myself are very pleased that, from the evidence of the above letters and of verbal comments, something has been initiated which a number of members feel to be helpful. A venture of this kind is necessarily experimental, and any comments on principle or on details may be of great assistance to later writers in the series.

I do not know whether I would agree completely with Mr. O'Brien's suggestion that there should be a segregation of the serious communication and the explanatory article. It may be that this would not further the end we have in mind of bringing together the practical man and the scientist. The trouble with the former is that he may be too much in a hurry, i.e. he wants to understand at first reading a paper which reveals its significance only after the sixth, but may then

have stimulated the reader to valuable thoughts of his own. The aim of my successors and myself is really to lay the train and light the fuse which will set off the explosive potentialities in the breast of every dyer. If this were done as a routine instead of a special occasion, two results might be foreseen—either we should run out of explosive breasts or we should all get used to the continuous noise. Guy Fawkes Day prolonged until August Bank Holiday might be a bit boring!

Dr. Nursten's bouquet contains a scarcely concealed brickbat. For those who have a morbid desire to plumb the murky shallows of my erudition, it may be suggested that a more accurate picture at least will be gained from other contemporary writings. Dyeing theory, after a period of neatness and logic, has gone fluid again. If it is desired to show a practical man the way in which a scientific problem is approached, an example which is full of ifs and buts may defeat its own object. Why not take a nice neat graphic theory which, when the article was first written, was also highly respectable? I cannot believe that, in its special context, it is likely to harm the scientific morals of either author or reader.

<div align="right">H. A. TURNER</div>

DEPARTMENT OF TEXTILE CHEMISTRY
   COLLEGE OF TECHNOLOGY
     MANCHESTER 1

1st February 1955

Papers on Nylon Dyeing by Pakshver *et al.*

When preparing an abstract of three papers [1-3] by Soviet authors on the dyeing of polyamide fibres, I noted that these papers, particularly the first, contain inaccuracies of such a nature that some form of published comment appeared to be desirable.

An examination of the abstract [4] will make the nature of some of these inaccuracies clear to those familiar with the literature of the subject, but some of these and other facts that cannot be derived from the abstract will be discussed here, mainly in the hope that the discussion will come to the attention of some of the workers, resident in most cases in territories where Soviet journals form the major direct source of information, who might be unaware of these discrepancies. This letter is not concerned with the original work on the dyeing of 6-nylon contained in these papers; this, while containing nothing that is new in principle, is undoubtedly a useful contribution to the subject.

The first of these papers, by Mankash and Pakshver [1], contains an analysis of the results of Munden and Palmer [5] on the effect of drawing on the dyeing of 6,6-nylon. Munden and Palmer's work on maximum equilibrium uptake, although broadly in agreement with "the stoichiometric relationship between the dyestuff and amine content of the nylon" [5], nevertheless indicates a fall in maximum equilibrium uptake with increasing draft. Mankash and Pakshver, however, state that Munden and Palmer obtained values that were independent of draft, and they give values, stated to be quoted from Munden and Palmer's paper, which are substantially in accord with this statement. They state also that Munden and Palmer give no explanation of these results, and they advance as an explanation, and present as a new discovery, the application of the Porai-Koshits theory of stoichiometric dyeing to polyamide fibres.

In actual fact Munden and Palmer lean on the already well established stoichiometric theory of the dyeing of nylon for support, making due reference, of course, to the work of its originator, Peters [6], which is not referred to by Mankash and Pakshver. Furthermore, Munden and Palmer's equilibrium uptake figures are incorrectly transcribed from their paper; thus, for Solway Blue BNS, the values (%) of these for increasing draft (0–260%) are 1·82, 1·65, 1·60, 1·60, which are quoted as 1·65, 1·60, 1·60, 1·60 respectively; in the case of Naphthalene Scarlet 4RS, the extreme difference in the figures is reduced by about one-third in transcription, and this reduced difference is then halved in a subsequent miscalculation into the form of the molecular weight of the fibre.

Mankash and Pakshver state also that Munden and Palmer give no explanation for the fact that the *rate* of dyeing depends greatly on the degree of draft of the fibre. This, again, is not true—Munden and Palmer give an explanation, and it is essentially the same as that given by Mankash and Pakshver (thus Munden and Palmer state: " . . . the dyeing rate depends critically on the diffusion process, which in turn is a function of the molecular orientation and order. High orientation and a high state of order hinder the dyestuff molecule in its progress to a suitable site" [5]; cf. abstract [4]).

It will be clear, therefore, that Mankash and Pakshver have misrepresented the contents of Munden and Palmer's paper and have also wrongly laid claim to the discovery of the application of the stoichiometric principle to nylon dyeing. The attribution of the theory of the stoichiometric dyeing of protein fibres to Porai-Koshits may also be disputed, although the contributions of this chemist to the development of the theory are probably sufficiently important for us to couple his name with that of its originator, Edmund Knecht, who propounded the theory in very clear terms and provided it with elegant experimental support as long ago as 1889 [7].

In addition to the inaccuracies detailed above, there are errors of a different character in this first paper, and some objections may be raised also to the discussions on "overdyeing" in the third paper. These I regard as of minor importance in relation to my purpose in writing this letter; detailed discussions of these have been forwarded to Prof. Pakshver. Some of these relate to the assumptions made in calculating the molecular weight of 6,6-nylon from Munden and Palmer's results— it is assumed that there is one free NH_2 per molecule (instead of ~0·4), that the dyes used were pure (they were "S" brands), and that each terminal NH_2 combines with one molecule of dye

acid, irrespective of the number of sulpho groups present in the molecule (in view of the evidence referred to by Munden and Palmer [8], and of other available evidence [9] with respect to 6,6-nylon, the use of the molecular weight instead of the equivalent weight would at least demand some justifying remarks in the text).

A. E. STUBBS

"ASHBOURNE"
   RADCLIFFE ROAD
      BOLTON

30th September 1954

[1] Mankash and Pakshver, *J. Appl. Chem. U.S.S.R.*, **26**, 976 (1953).
[2] Myagkova, Pakshver, and Frolov, *ibid.*, **26**, 991 (1953).
[3] Mankash and Pakshver, *ibid.*, **26**, 1200 (1953).
[4] J.S.D.C., **70**, 520 (Nov. 1954).
[5] Munden and Palmer, *J. Textile Inst.*, **41**, P 609 (1950).
[6] Peters, J.S.D.C., **61**, 95 (1945).
[7] Knecht, *Ber. dtsch. chem. Ges.*, **22**, 1120 (1889).
[8] Abbot, Crook, and Townend, J.S.D.C., **63**, 462 (1947).
[9] McGrew and Schneider, *J. Amer. Chem. Soc.*, **72**, 2547 (1950).

In his critical letter relating to three of my papers from the *Journal of Applied Chemistry (U.S.S.R.)* of 1953, Dr. Stubbs points out errors made by me and my co-workers in the calculation of the molecular weight of 6,6-nylon from the data of Munden and Palmer. Dr. Stubbs maintains that my papers contain nothing new in principle that was not known from the English literature. In addition to this letter, Dr. Stubbs has kindly sent me some further information which clarifies his viewpoint.

After taking note of Dr. Stubbs's letter and the information sent by him, I wish to make the following points—

1. It is true that in calculating the molecular weight of 6,6-nylon from the data of Munden and Palmer I made an error, which may be explained by— (*a*) I am not a specialist in organic dyes, and am not acquainted with the significance of the brands of these dyes used in England; (*b*) only a translation of Munden and Palmer's paper was available to me, and this evidently contained errors in the values given in the tables.

Hence, my calculated values for the molecular weight of 6,6-nylon are incorrect.

2. The objections referred to in Dr. Stubbs's letter against the equality of the equilibrium amounts of sorbed dye for stretched and unstretched 6,6-nylon appear to be of doubtful validity. According to my own laboratory results on stretched and unstretched Capron [6-nylon], the equilibrium amount of bound dye is always the same (in absence of other reactions).

3. Dr. Stubbs's objections to the calculation of the molecular weight of 6,6-nylon from the molecular weight (instead of the equivalent weight) of the dye are again not always valid. According to my results, some acid dyes that have two sulpho groups react with the amino groups of nylon through only one sulpho group, the behaviour observed depending, apparently, on the spatial structure of the dye.

4. Dr. Stubbs's objections are based on only one of the three papers cited— Communication No. 3 [i.e. the first]. These objections cannot in any way affect the fundamental content of my papers or my conclusions, for I used dyes and other organic compounds that contained only one sulpho group, and the molecular weight determinations refer to Capron in which only free amino groups occur. The molecular weight calculations for 6,6-nylon from Munden and Palmer's data should serve merely as an illustration of the ideas under discussion in my paper.

5. Nowhere in my papers have I asserted that I have made a discovery that is new in principle. It is well known to me that general views on the effect of fibre structure on the rate of diffusion of dyes have been expounded previously by British investigators (Munden and Palmer, Peters, *et al.*) and German workers (Elöd and co-workers). At the same time, as far as I know, no-one previously has attempted to express fibre structure by means of diffusion coefficients calculated mathematically. Also, no attempts have been made to explain this difference by the presence of intermolecular hydrogen bonds. Simultaneously with mine, analogous attempts were made by a British school of physical chemists (Park, Long, *et al.*) for polymer films, and only quite recently (Summer 1954) a paper appeared in the *Melliand Textilberichte* on the diffusion of dyes in polyamide fibres.

A. B. PAKSHVER

IVANOVSKIĬ KHIMIKO-TEKHNOLOGICHESKIĬ INSTITUT
  IVANOVO
    U.S.S.R.

24th December 1954

Gas Fume Fault on Wool

It surprises us very much to learn that this matter has not been previously reported in the *Journal*[1], as it is a problem which we have known to occur at quite regular intervals, and we normally look for it as a routine check when investigating alleged "fades".

In our experience the incidence of gas fume fading may occur on any dyed wool textile where an anthraquinone blue has been used as either a blue or a green–blue or even as a compound shade — fawn, slate, green, nigger, etc. From our observations it appears to us that, although occurring in warehouses as found by Mr. Bird, it shows up most frequently in cases where the dyed goods have been on display in shop windows where gas radiators or even gas burners have been used to prevent or remove condensation and steaming up of the plate glass. Such instances would be expected to be most marked during the winter months, and such proves to be the case.

We feel that the attendant moisture *and* light play a big part in this problem; patterns exposed to gas fumes in the *absence* of light do not appear to have exactly the same hue or degree of fading as the goods complained of, or as the normal pattern exposed to the fumes in the presence of daylight. The discrepancy is shown up readily under ultra-violet radiation. We refer throughout to actual burnt coal gas fumes.

It is thought probable that some salt formation takes place between the amino groups of the dye and the nitrous acid, and that this is hypersensitive to light, particularly under very moist conditions. In actual fact we have found the Blue B type of dye to be commonly present, but this may be due to its very wide use.

Incidentally, if a pattern is prepared to contain a residual amount of sulphamic acid, it seems to be able to resist to some degree the attack of burnt gas fumes. This might have some bearing on the work done some time ago on the effects of nitrites on alizarin blues, in which these dyes were shown to be very sensitive to, and even to be destroyed by, minute traces of nitrites in water, but only under acid conditions as in acid dyebaths, etc. It was claimed that this effect was inhibited by urea and sulphamic acid [2].

Finally, we have found this gas fading effect on such widely variable goods as knitting yarns in hanks, ladies' woollen dress goods, and even made-up garments of fast and union dyed cavalry twill type of riding attire (in drabs, etc.). Thus it would appear that even some of the neutral-dyeing dyes are not completely free from suspicion in the presence of nitrous acid, etc. from burnt gas fumes.

D. HOLGATE
for ANALTEX

BAILDON
  SHIPLEY
    YORKSHIRE

31st January 1955

[1] Bird, J.S.D.C., **71**, 46 (Jan. 1955).

[2] Campbell and Twemlow, *Interesting Data relating to Acid Alizarine Blues—The Effect of Traces of Nitrous Acid* (Huddersfield: L. B. Holliday & Co. Ltd.).

Adsorption of Brazilwood and Logwood Colouring Matters by Fibres

I should like to make the following comments on the paper by C. H. Giles and his co-workers [1], apropos the testing of logwood products by trial dyeing.

The method of testing by dyeing on patterns of wool mordanted with "oxidising" and "reduced" chrome mordants, which was used in this work, is practically obsolete, and only a fully reduced mordant is usually employed. On this mordant, haematein is determined by direct dyeing, and haematein plus haematoxylin by dyeing with addition of predetermined quantities of sodium nitrite and acetic acid, in comparison with a standard product of known strength. The method is tedious, but, in experienced hands, is capable of giving a much higher degree of accuracy than the older method.

The assumption underlying the testing of logwood products is not that only haematein is adsorbed by a reduced chrome mordant, as stated in the paper, but that haematoxylin does not form a coloured lake. This assumption would not be justified if pure haematoxylin were used, owing to the readiness with which it is oxidised to haematein, but commercial logwood products are much more stable than the pure compounds in this respect, and no difficulty arises from oxidation by air during the period required to make the tests.

O. NEWSOME

THE WEST INDIES CHEMICAL WORKS LTD.
  1 BRAZENNOSE STREET
    MANCHESTER 2

17th February 1955

[1] Arshid, F. M., Desai, J. N., Duff, D. J., Giles, C. H., Jain, S. K., and Macneal, I. R., J.S.D.C., **70**, 392 (1954).

ERRATA

Metallic Pigments. G. W. Wendon (J.S.D.C., **71**, 125 (March 1955))—The date of the meeting should be 14th January **1954**.

Naphthaquinoneimine Disperse Dyes. Celanese Corpn. of America (J.S.D.C., **71**, 156 (March 1955))—In the last line "oil" should be **ice**.

Notes

Meetings of Council and Committees March

Council— 9th

Finance— 9th

Publications— 15th

Diplomas Executive Subcommittee— 23rd

Colour Index Editorial Panel— 17th

Fastness Tests Co-ordinating— 1st

Perkin Centenary— 4th

Perkin Centenary Executive— 28th

Joint Finance and *Colour Index* Panel— 22nd

Deaths

We regret to report the loss by death of Mr. R. C. Collinge, Mr. G. H. Frank, and Mr. W. W. White.

Tentative Withdrawal of Approval of FD&C Orange No. 1 and 2 and FD&C Red No. 32

The U.S. Department of Health, Education, and Welfare has issued a tentative order withdrawing the approval of the Food and Drugs Administration to certification of FD&C Orange No. 1, FD&C Orange No. 2, and FD&C Red No. 32. FD&C Orange No. 1 is largely used in the U.S. sweets and confectionery industries, and has the biggest sale in the U.S. of any certified coal-tar dye. The other two dyes are chiefly used for colouring oranges.

C. O. C.

U.K. Production of Antimony Oxide Pigments

According to the British Bureau of Non-ferrous Metals Statistics, 1,735 tons of antimony was used in 1954 for making antimony oxide pigments, an increase of 96 tons on the amount used in 1953.

C. O. C.

CIBALANS

In Vigoureux Printing.

Prints of high fastness to washing, milling, and light are obtained with Cibalans, no chrome mordants being necessary. In contrast to the chrome dyes, they are reliable and simple in application. Printing pastes show unlimited stability, giving maximum colour yield and uniformity of shade. The steamed slubbing can be washed off easily in a three-bowl back washer.

and for fast dyed shades on wool, silk, nylon and other polyamide fibres

CIBA

CIBA Limited, Basle, Switzerland

The Clayton Dyestuffs Co. Ltd., Manchester 11

Sole Concessionaires in the United Kingdom

Inns and the Textile Trade

No. 2 *'The Yutick's Nest' — Dickinson St., Blackburn*

And what, you have every right to ask, is a yutick? No encyclopædia will define it—most ornithologists would ask you how to spell it.

According to tales told in Lancashire, there are two species of yutick — both nearly extinct. The original one is a rare Australian bird that has lost the use of its wings. The other is a millworker. 'Yutick' is an old Lancashire slang term for a loomer or drawer-in . . . a fortunate fellow who could do his work on the spot and who, like the bird, did not 'fly about'.

The public house in Blackburn which bears the unique name of the 'Yutick's Nest', was until the end of the last century known as the 'Bricklayer's Arms'. Then a local man, John Fish, became the licensee. He had been a yutick, his sons were yuticks and his house became the popular retreat of fellow yuticks. He consequently arranged to have his hotel renamed more aptly 'The Yutick's Nest'.

Much has changed since then. The millworker today earns a good living in far better conditions; the modern public demands harder wearing and in many cases specially processed materials with fast non-fading colours. The chemical research that strives to meet these demands is conducted by companies like Brotherton.

Brotherton

Centenary of the Textilingenieurschule in Krefeld

The centenary of the founding of the School of Textile Engineering in Krefeld, Germany, is to be celebrated in October 1955 by a reunion of former students, both German and foreign. Since the School's registers have been lost as a result of the war, former students are requested to inform the School authorities, by 1st May 1955, of their present address, years in which they attended the school, business address, and position held. An invitation and a memorial volume will then be sent to them. The address is Textilingenieurschule, Krefeld, Adlerstrasse 32, Germany.

Centenary of the Staatliches Technikum für Textilindustrie, Textilingenieurschule in Reutlingen

The centenary of the above institution will be celebrated at Reutlingen, Germany, on 27th May 1955. Former students are requested to forward their addresses, so that an invitation and the programme can be sent to them.

OBITUARY NOTICES

John Thomas Kidd

We regret to record the death of J. T. Kidd on 6th December 1954, at the age of fifty-five.

After leaving Leeds Modern School, J. T. Kidd joined the army and served in France as an officer of the K.O.Y.L.I. On his return to this country he became a student in the Department of Colour Chemistry and Dyeing at Leeds University, where he obtained the degrees of B.Sc. in 1922 and M.Sc. in 1923.

He then joined the staff of British Celanese Ltd. at Spondon, but left in 1925 to become chief chemist and technical manager for the Norwich Silk Mills. After five years in Norwich he became general manager to the British Silk Dyeing Co. Ltd., Balloch. During his stay in Scotland he took an active interest in local affairs and was appointed a member of the Board of Governors of the Henry Brook Hospital at Alexandria and a member of the Juvenile Employment Advisory Committee for Dunbartonshire.

After leaving Scotland he went to Samuel Heap & Co. Ltd., Rochdale, as manager of their "Old Mill". Following a period of ill health, he joined the staff of the Bleachers' Association Ltd., and for the last seven years of his life was employed as chief chemist at their Heaton Mersey branch.

J. T. Kidd joined the Society as a Junior Member in 1920. He was a member of the Scottish Section Committee from 1932 to 1935 and a member of the Publications Committee from 1943 to 1950. From 1943 onwards he was an examiner for the City and Guilds of London Institute. He was elected a Fellow of the Society in April 1954.

He leaves a widow and one son.

C. L. BIRD

Alfred William Dudbridge

Many members of the Society learnt with deep regret of the passing of A. W. Dudbridge, who had been a member since 1916, and had occupied several offices in connection with the West Riding Section Committee, ultimately becoming Chairman. Afterwards he was a Vice-president of the Society from 1949 to 1952.

He carried out his duties in these various offices sincerely, ably, and in an unassuming manner that endeared him to all his friends, for the keynote of his character was a strict sense of duty in all walks of life.

It was his deep interest in the art of practical dyeing that led him to become associated with the Guild of Technical Dyers, and he held the position of President and Trustee of that body during his long term of membership.

His technical training was received at the Technical College, Bradford, and he was apprenticed to his brother, the late Mr. A. B. Dudbridge (also an old and esteemed member of the Society), with whom he worked for several years. After that training he was employed in 1903 as Foreman Dyer by a firm of silk dyers and finishers in Kent. In 1905 he returned to the West Riding as Technical Dyer to Messrs. Abraham Moon & Sons Ltd., Woollen Manufacturers, Guiseley, with whom he was associated up to the time of his death.

His ability, sterling character, and trustworthiness in all his work and dealings were finally recognised by his appointment to the Board of Directors of the above company in 1953, for he always enjoyed their confidence and had their interests at heart.

During the many years he was connected with the dyeing trade he developed a remarkable intuitive sense relative to technical matters and difficulties that are met with almost daily in the running of a dyehouse, and this contributed largely to the success of his work.

Alfred Dudbridge will be remembered by all his many friends as a man of the highest integrity, kindly and considerate to all, in whatever station of life, and one who had a natural and genuine desire to help and serve his fellow men.

A. C. WALSH

New Books and Publications

Review of Textile Progress
Volume V, 1953

Published jointly by the Textile Institute and the Society of Dyers and Colourists. Pp. 588. Price, 35s. 0d. (28s. 0d. to members of the Institute or the Society).

The last three issues of the *Review of Textile Progress* suggest that it has now settled down to a standard size and price. Not every topic is covered each year, and in the current volume chapters on cotton production, felt, and physical testing reappear, whilst bast fibres and carpets are omitted. The longest individual chapters are, as usual, those dealing with dyeing and with the finishing of fabrics other than wool.

Any review of recent advances in a branch of technology tends to become an abstract of abstracts, and the authors who have dealt with the chemistry of synthetic-polymer fibres and with dyeing are to be congratulated on their efforts to provide some clothing for the bare facts.

In his Introduction, the Chairman of the Joint Committee has drawn attention to two trends, viz. the developing interest in synthetic fibres outside the U.S.A. and Western Europe, and the attempts which are being made to improve cotton fibres by chemical treatment and cotton fabrics by novel resin finishes.

Only a small part of this *Review* can be said to be outside the scope of the Society, and its value to members can no longer be questioned.

C. L. BIRD

Textile Terms and Definitions

Manchester: The Textile Institute. 1954. Pp. 46. Price, 5s. 0d.

This is a compilation in alphabetical order of definitions of some five hundred textile terms, some of which are merely tentative, whereas others have been formally adopted. Most have already been published in the *Journal of the Textile Institute*. Several definitions have been discussed with the Society's Terms and Definitions Committee. The booklet concludes with a proposed classification of textile fibres. C. J. W. H.

The C.I.E. Colour System explained

By G. J. Chamberlin. Pp. 34. Salisbury: The Tintometer Ltd. 1951. Price, 5s. 0d.

The feasibility of matching a colour by a controllable, additive combination of three primary colours is one of the oldest concepts of physiological optics, and is now widely appreciated in principle, if not in detail, in the colour-using industries. That the precise nature of the three chosen primaries is unimportant is also recognised, and the main virtue of the C.I.E. (Commission Internationale de l'Éclairage) system is that it renders unnecessary the use of a multitude of colour reference systems by individual investigators, by specifying three primary stimuli which are algebraically convenient, and to which any experimental data can be referred. Its physical significance is no greater, however, than that of the experiments carried out in the late 1920s by Wright and Guild, and in fact the C.I.E. system is merely a mathematical manipulation of these data.

It is not surprising, therefore, that the declared intention of this booklet, which is "to explain in non-mathematical and non-technical terms the basis of the C.I.E. convention", is not fulfilled. It is never possible to explain mathematics in non-mathematical terms, but a good deal of the sense may be conveyed by analogy if the latter is well chosen. It does not seem possible, however, adequately to cover the basic theory of the colour triangle, additive and subtractive colorimetry, the chromaticity and uniform-chromaticity diagrams, and many other aspects of colour theory within the compass of a small booklet, whatever the method chosen.

The inevitable result is that the reader is left with little idea of the relative importance of the various concepts dealt with. For instance, four pages are devoted to the controversial subject of uniform chromaticity and four lines to the basic concept of chromaticity co-ordinates and their definition.

A good description of the properties of colour triangles is given which should be both intelligible and instructive to the newcomer to the colour field.

E. ATHERTON

An Old Silk Family 1745–1945
The Brocklehursts of Brocklehurst-Whiston Amalgamated Ltd.

By Mary Crozier. Pp. 45. Aberdeen: The University Press. 1947. [No price.]

A copy of this interesting and beautiful book, bound in blue figured silk made in the mills of Brocklehurst-Whiston Amalgamated Ltd., has been presented to the Historical Records Committee of the Society.

The book opens with ten photographs of the Brocklehurst family, which had an unbroken connection with the silk trade from 1745 to 1911, and the story of this family reflects the progress of silk manufacture in this country.

It was in 1745 that John Brocklehurst joined the firm of Acton & Street, button manufacturers, in the building now occupied by the offices of the Hurdsfield Mills. Silk buttons had been in use since about 1600 and, in an attempt to encourage the silk-button trade, Parliament, in 1720, passed a law forbidding anyone to wear buttons covered with the same material as the garment to which the buttons were attached. It looks as though this legislation was unable to save the industry, for horn and brass buttons became popular, and by 1749 at least one of the Brocklehurst family described himself as a "silk merchant".

In 1766 the Bailiffs, Wardens, Assistant, and Commonalty of the Trade, Art, and Mystery of Weavers of London, on behalf of themselves and

the silk manufacturers of Great Britain, complained of the great decline in trade owing to the legal (and illegal) importation of "Foreign Wrought Silk".

A Macclesfield throwster, in giving evidence at the same time, provided an important estimate of the work done in the town in trades allied to silk-throwing. He stated—

In proportion as this business declines, many People will be deprived of Work, who are not employed in Throwing Silk, as he believes from 12 to 15,000 People are employed in working up the Waste, which is made into Ferrets, Stockings, Knee Garters, Fringes and Sewing Silks; which Trade would be ruined with the Throwsters; and there has not been a sufficient Quantity of Waste lately to supply the Demand.

The weekly wages in 1776 were— stewards 7s.; mill men 7s.; women doublers 3s. 6d.; children (hired for three years) 6d. during the first, 9d. during the second, and 1s. during the third year.

One branch of the family took up banking, and the original "Bankers License in England" dated 1816 still exists. Another Brocklehurst entered Parliament, giving evidence in 1832 that the silk trade declined between 1824 and 1832 from 276,000 to 117,000 spindles and from 10,229 mill hands to 3,622. He indicated that the hours of work were from 6 a.m. to 12 noon with twenty minutes off at 8 a.m. for breakfast, then an hour for dinner, and work again from 1 p.m. till 6 p.m., with sometimes twenty minutes for tea at 5 o'clock. Employees were allowed to work two hours extra if they wished.

During the Chartist riots the firm did not suffer severely, possibly because of the iron windows and doors which the firm fitted to guard against trouble. These may still be seen.

The firm possesses an original Indenture of Apprenticeship dated 1842 binding the apprentice for a period of five years, during which time he must "well and faithfully serve, demean and behave himself and keep his Master's secrets". He was not to waste, damage, or lend any of his master's goods; nor play cards, dice, or any unlawful games; nor haunt gaming houses, taverns, ale houses, or disorderly houses of any kind; nor was he to exercise the said trade or mystery on his own account. He was to work 14 hours a day except Sundays, and was to have one hour each day for dinner.

Six coloured illustrations of silks woven by the firm in the first half of the nineteenth century are included, and at least one was shown in the London Exhibition of 1853. The beautiful colours are all the more remarkable in view of the fact that they were produced before the discovery of coal-tar dyes. The volume includes in addition twenty photographs of historical buildings and documents and six coloured plates of old English costumes.

It is interesting to note that, although the firm never advertised until 1911, it held contracts for the supply of black silk handkerchiefs for the Navy and had a monopoly of satins for Liberty's as well as of silk for Malta lace.

In 1929 J. & T. Brocklehurst Ltd. amalgamated with the hand-block and screen printing firm of William Whiston & Son Ltd. of Langley near Macclesfield, thus cementing the close association and friendship which had existed between the two firms for so many years.

The Society is indeed fortunate to have acquired a copy of such an interesting book, which will have a special appeal to the historian as well as to anyone interested in the silk industry.

A. THOMSON

Brocklehurst-Whiston
The Story of its Activities

3rd edition 1952. Pp. i + 64. Macclesfield: Brocklehurst-Whiston Amalgamated Ltd. [No price.]

While this booklet is primarily produced with the object of giving boys and girls leaving school some idea of the many operations which silk undergoes during processing and manufacture, it is sure to interest anyone concerned with textile operations in general and silk materials in particular. It is well written, and its many excellent illustrations show clearly the different stages in the production of dyed and printed silks.

Messrs. Brocklehurst-Whiston are to be congratulated on an excellent publication which cannot fail to attract the right type of entrant into the industry. A. THOMSON

Mechanism of Polymer Reactions

By G. M. Burnett. Pp. xv + 493. New York and London: Interscience Publishers. 1954. Price, 80s. 0d.

Of books on high polymers there is no end. Just as M. Jourdain was brought to realise that he had, quite unwittingly, been speaking prose all his life, so have we, in the last few decades, perceived that most of the everyday organic matter around us— wood, textiles, rubbers, proteins, carbohydrates— is composed of high polymers. As a result of the intensive research into such compounds during the past thirty years, traditional industries have been revolutionised and new ones called into being.

A natural concomitant of the intensive research is an annual output of several hundred scientific papers dealing with the mechanism of the formation of high polymers alone. Under such conditions, the need for well written textbooks which will summarise recent developments and present them from a unified viewpoint is urgent. Unfortunately, textbooks, even if written with abnormal pre-science, quickly become out-of-date in this field, and such a fate has overtaken an old favourite, Mark and Raff's *High Polymeric Reactions*. This, the third volume of Interscience's series of monographs on High Polymers, has been revised, or rather completely rewritten, by Professor G. M. Burnett, having its title changed in the process.

In its new guise, Volume III is likely to prove of great interest to those interested in the fundamental mechanism of polymeric reactions. Mark and Raff's book was divided into a general section, dealing with experimental method and theory, and a

special section, in which practically the entire literature was abstracted, monomer by monomer. Professor Burnett's book really consists of a 100% expansion of the former general section, although the polymerisation of some of the commoner monomers is described in some detail by way of illustration.

An unusual feature of this highly individualistic book is the detailed mathematical approach used in many chapters. This results in some pages having a rather forbidding appearance to those who do not like the Greek alphabet, but in reality conceals a great simplification. Every step is clearly set forth, often more extensively than in the original publication, thereby rendering a great service to those of us whose mathematical knowledge is limited. A chapter on gas-phase polymerisations is a unique feature, and several kinetic analyses are published here for the first time. Considerable emphasis is given to the contributions of Professor Melville's school, of which Professor Burnett was a distinguished member for ten years, but, as Professor Flory explained in the preface to his own excellent book on polymers, it is difficult to write from any viewpoint but one's own! The printing is pleasant, and although several minor misprints were noticed, no serious mistakes were seen. The only statement to which the reviewer took exception was the affirmation on p. 406 that polyacrylonitrile loses hydrogen cyanide during the colour changes developed in thermal degradation, as he was under the impression that hydrogen was evolved.

Practically the whole of the work is concerned with vinyl polymerisations, and linear condensation polymers occupy only nine pages. It will thus be seen that this book is not likely to be of much service to practical dyers and finishers, but will be read with pleasure and instruction by those engaged in research in this field and can be recommended to those who wish to learn the "know-why" of polymeric reactions.

L. VALENTINE

Technique of Organic Chemistry
Volume I
Physical Methods of Organic Chemistry
Part III

Edited by A. Weissberger. 2nd edition 1954. Pp. xi + 2097–2530. New York and London: Interscience Publishers. Price, $8.50.

A second edition of Weissberger's *Physical Methods of Organic Chemistry*, comprising Parts I and II, appeared in 1949 (cf. J.S.D.C., **67**, 118 (1951)). Since then, new methods have developed to a state warranting inclusion and established methods have been extended. Part III, including such new methods and additional material on others previously dealt with, is intended to supplement and rejuvenate the second edition. It follows the general pattern of Parts I and II, an account of each method, generally comprising theory, technique, and in some cases applications, being contributed by an expert or experts. The new topics are—electron microscopy, microspectroscopy,

determination of streaming birefringence, measurement of dielectric constant and loss, radio-frequency spectroscopy, and neutron diffraction. Sections dealing with viscometry of dilute polymer solutions, X-ray and electron diffraction, magnetic susceptibility, and determination of radioactivity by scintillation counting appear as supplements to accounts given in Parts I and II.

Some of the material will be of considerable interest to the chemist concerned with dyes and textile materials. Under "Electron Microscopy" are to be found details of its application to the study of fibres, dyes, synthetic high polymers, soaps, and greases. It is rather surprising, however, to find no mention of European work on the electron microscopy of fibres. Almost all the references in this section are American and they are not always readily accessible. Microspectroscopy is a method of obtaining spectra of very small samples and can be applied to the study of individual fibres. Details of instruments and techniques used in ultraviolet, visual, and infrared microspectroscopy are given. Fibres are said to be particularly adapted to examination in the infrared spectroscope, and the spectra obtained with certain fibres may provide information on the configuration of polypeptide chains.

The sections on streaming birefringence, dielectric constant, radio-frequency spectroscopy, and neutron diffraction, concerned mainly with theory, apparatus, and techniques, seem of less interest to the dyer or textile chemist. Streaming birefringence studies can, however, provide information on the configuration of high-polymer chains in solution and, although this is not specifically mentioned, dielectric constant measurements have been used to study bonding between dyes and fibres and the shapes of polymer chains in solution.

Of the supplements to sections in Parts I and II, that on the viscometry of dilute polymer solutions may be of most interest. The dependence of viscosity on concentration and on molecular shape of polymer and the influence of solvent are discussed. Under the latter heading the thermodynamic measurement of solvent power and its correlation with viscometric measures are considered. Consideration is, however, almost entirely restricted to solutions of flexible polymers, and the lack of applicability of such viscometric measures to solutions of cellulose and its derivatives is not mentioned. There is a very brief consideration of the recent Fox–Flory treatment of viscosity.

The supplements on X-ray and electron diffraction deal mainly with interpretation of results. That on magnetic susceptibility includes some applications to high polymers such as polyethylene terephthalate and polystyrene, leading to interpretation of the anisotropy of chains in fibres. The supplement on determination of radioactivity by scintillation counting is concerned mainly with apparatus.

Printing and arrangement are good, and the level of the contributions to Parts I and II has been maintained. The book is well documented with

references and there are many clear diagrams. All chemists possessing Parts I and II will find this part a welcome addition. W. R. MOORE

Organic Analysis
Volume II

Edited by J. Mitchell, I. M. Kolthoff, E. S. Proskauer, and A. Weissberger. Pp. viii + 372. New York and London: Interscience Publishers. 1954. Price, $8.50.

This volume is the second of a series designed to acquaint chemists with reliable and critical information on general methods for the analysis of organic systems.

Volume I was devoted almost entirely to methods of functional group analysis. In the present volume more emphasis is placed on techniques. Of the nine chapters, the first three are devoted to the determination of functional groups— viz. microdetermination of carboxyl groups (Steyermark); determination of esters (Hall and Shaefer); and determination of nitro, nitroso, and nitrate groups (Becker and Shaefer)— whilst the remaining six describe techniques which may be used for the determination of many kinds of functional groups— viz. applications of lithium aluminium hydride to organic analysis (Higuchi); coulometric methods (Cooke); application of polarography to organic analysis (Elvin); methods based on reaction rate (Lee); phase solubility analysis (Mader); and countercurrent distribution (Weisiger).

As with the first volume, the book is written for a wide audience and contains material which is of value both to the experienced analyst and to the student, provided, of course, that both groups make allowances for the needs of the other.

The general method of presentation which was adopted in Volume I has evidently proved satisfactory and is retained. A general theoretical background is given first in each chapter, and is followed by a description of experimental methods and examples. There is, however, a difference between the two sections into which the book divides itself. In the chapters dealing with functional group analysis, descriptions of the analysis of a number of specific substances by one or other method are given in some detail. In the chapters devoted to techniques, the treatment is far more general, and the reader is led, naturally, to devising means of adapting the various procedures to his own problems. This may be taken as a measure of the efficiency with which the authors have done their job.

A general criticism of the first three chapters, as with Volume I, is that the authors have, at times, taken detail too far. Thus the statement that "the flow of solution from the burette is controlled by means of a glass bead in a rubber tube, a pinch clamp or a ground glass stopcock" is out of place for those likely to read a book of this standard.

In the chapters dealing with techniques a larger proportion of the space has rightly been given to theoretical considerations. Unfortunately, however, these sections are not always as clearly

written as might be desired. For example, in the chapter on phase solubility analysis the important fact, on which the method largely depends, that the slopes of some branches of the phase diagram represent the concentrations of some of the constituents of the mixture being analysed, is not stated clearly and becomes obvious only after several examples have been given.

However, these things apart, the book is well written, the material being presented in a logical way and well printed up to the standard associated with the publishers. For those who wish to pursue any topic further ample references to the original literature are given— almost eight hundred in all. A cumulative index to Volumes I and II is provided at the end. A. JOHNSON

Guide for Safety in the Chemical Industry

Prepared by the General Safety Committee of the Manufacturing Chemists' Association Inc. (Washington D.C.). Pp. xiii + 234. New York: D. Van Nostrand Co. Inc. 1954. Price, 32s. 0d.

This publication, which puts forward the considered recommendations of the American Manufacturing Chemists' Association, contains many excellent illustrations and in its thirteen chapters seeks to compress the greatest range of information in the smallest possible space. The subject-matter is grouped under the following headings— general rules for laboratory safety; laboratory design and equipment; handling and storage of glassware and containers; hazards— chemical, pressure vessels, and miscellaneous; inflammability and toxicity, with tables of safe (or unsafe) limits; laboratory first-aid and suggestions for medical treatment; packaging and transport of chemicals; radioactive chemicals— safety and contamination control in the laboratory.

Frequent references are made to individual data-sheets issued by the Association as guides for the safe handling of well known chemicals, to U.S. Government publications, and to manuals of standard and recommended practice.

The chapter on packages and transport of chemicals deals mainly with regulations governing transport by mail, public transport, and air in the U.S.A., but, as similar regulations are issued in other countries, the chapter is not without interest to readers in other lands.

In short, the publication has collected under one cover an abundance of valuable information. Much is, or should be, already known to workers in laboratories, but as so much is regularly overlooked or ignored, repetition can only be of great value.

The contents of the chapter dealing with the precautions to be taken when working with radioactive chemicals present matter probably new to most laboratory workers, but deal with a subject which is becoming of rapidly increasing scope. It is, therefore, important that a guide for safety should give the latest information on the precautions to be taken when dealing with chemicals of this type. H. B. BRIGGS

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, 23 (*Jan. 1952*), *and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Mechanical Aid for Wet Processing in the Finishing Industry—the Turbinator. J. Häusermann and E. Hablützel. *Textil-Rund.*, 9, 621–628 (Dec. 1954); also *Melliand Textilber.*, 36, 65–68 (Jan. 1955).

Experiments have been made with an oscillatory turbine rotor designed to increase mechanical action in the wet processing of fabrics. A model jig was used to study the effect of the increased mechanical action in (a) dyeing cotton fabric and nylon fabric, (b) washing standard soiled fabric, and (c) washing cotton fabric free from caustic soda solution. In all cases the increased mechanical action gave better results than the controls carried out under normal conditions. A full-scale vat dyeing of a cotton poplin in a commercial jig fitted with a turbine rotor showed quicker dye uptake and greater final depth of colour than the control. The improved dyeing effect may show up any latent unevenness in the fabric. Illustrations of the dyed patterns are reproduced. The theory underlying the action of the turbine rotor is discussed, and the possible range of its applications is briefly considered.   J. C. F.

PATENTS

Treating Yarn with Liquids. N. V. Kunstzijdespinnerij Nyma.   BP 720,975

Two rows of baffle plates extend inwardly from the side walls of a trough or channel, one row from each side wall, and define a slot in it which receives the yarn. The baffle plates are inclined with respect to the rear wall of the trough. When used for continuous treatment of yarn no difficulty is met with in keeping the liquid in the trough.   C. O. C.

Supports for Yarn Packages while being Wet Processed. Wilhelm Geidner Metallwaren-fabrik.   BP 721,922

A support which increases the mechanical stability of the packages and is suitable for both conical and cylindrical cross-wound packages.   C. O. C.

Package Drying. Metropolitan-Vickers Electrical Co.   BP 722,116

The packages are first treated with hot air, then with high frequency dielectric heating and finally with hot air. This gives relatively rapid drying for the cost involved.   C. O. C.

Electrical Wet Heat Treatment of Materials having Poor Electrical Conductivity. E. B. Bates.   BP 721,352

The material, e.g. fabric, is wetted out with a conducting liquid and then led into direct electrical and physical contact across its whole width with a number of electrical conducting members in turn. These members are arranged alternately to engage opposite faces of the material and are energised so as to cause an electric current to pass through the material during its passage past them. This current is large enough to bring the liquid in the material to the boil by resistance heating. Boiling takes place in and on the material in the region between the electrodes but not in their immediate vicinity. The process has wide applications, e.g. for scouring knitted fabric without disturbing the loops or fibres or for bleaching by impregnating with brine when if D.C. is used or D.C. imposed on A.C. nascent chlorine is liberated, wool fabrics treated in such a manner are rendered less liable to felt. C. O. C.

Screen Printing Machine. Reggiani Meccanotex.   BP 721,797

A machine embodying means for advancing the cloth in such a manner that it is exactly advanced and/or stopped at each printing step.   C. O. C.

Dryers. T. Strattner and A. Grimm.   BP 722,033

Hot air is blown perpendicularly on to the material through nozzles evenly spaced over the whole width of the dryer and is then exhausted through corresponding channels. One or more ribbed heating pipes is or are mounted at least mainly within backwardly diverging portions of each nozzle. This makes very efficient use of the heat consumed.   C. O. C.

Drying Hosiery. Smith, Drum & Co.   USP 2,669,788

A machine for the continuous drying of batches or bundles of stockings.   C. O. C.

Roller Hardener for Felts. American Felt Co.
BP 722,490
BP 722,499
BP 722,500

A roller hardener in which sufficient hardening is obtained in one run.   C. O. C.

Applying Several Treatments to Hides as a Continuous Process. Tanners' Research Corpn.
USP 2,669,111–2

A machine for automatically subjecting hides to a number of treatments, e.g. unhairing, scudding, checking and fleshing, compensation being automatically made for varying sizes and thicknesses of hide. All the operations are carried out by fluid pressure.   C. O. C.

Fur Skin Drier and Stretcher. E. Schulz.
USP 2,669,057

A drying and stretching frame especially suitable for use with mink and similar skins of different sizes has a pair of longitudinal side rods, having sliding hooks on them which can be fastened to the hind feet portions of the skins to hold them in position.   C. O. C.

Bronzing Machines. Soldana.   BP 720,641

A plush-covered feed or duct roller is in contact with a powder trough, one wall of which is formed by a flexible and retractable blade whose free end bears against the plush. This blade is differentially adjustable along its length relative to the roller so that the density of the spray of powder delivered from the roller as it rotates can be varied as desired along the length of the roller. C. O. C.

Detecting Bowing in Rotating Cylinder or Rolls and Straightening Rotating Cylinder or Rolls by Controlling the Bowing when detected. Pilkington Brothers.   BP 723,219

Calender for Turning Plastic into Sheets. Farrel-Birmingham Co.   BP 722,531

A calender which turns out very thin sheets of uniform character.   C. O. C.

Calender for forming Plastic Sheeting of Uniform Thickness. Wingfoot Corpn.   BP 723,041

The crown of at least one of a pair of co-operating rolls can be adjusted during operation thus rendering it possible to obtain uniform thickness in the sheets of material being worked by the rolls.   C. O. C.

Quench Section for a Carbon Black Furnace. Phillips Petroleum Co.   BP 723,187

II— WATER AND EFFLUENTS

Water Purification in the Textile Finishing Industry. O. Reichling. *Textil Praxis*, 9, 1187–1192 (Dec.1954).

A review of methods of water purification including the removal of dissolved oxygen, carbon dioxide, hydrogen sulphide, insoluble matter, oils, silica, acids, iron, and hardness.   B. K.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Sulphonation and Sulphation. J. P. Sisley. *Amer. Dyestuff Rep.*, 43, 741–748 (8 Nov. 1954).

A survey is presented of the mechanism and the scope of sulphonation and sulphation reactions involving saturated fatty acids, unsaturated fatty acids with one double bond, and unsaturated hydroxy acids, including the formation of hydroxy acids, complex hydroxy acids, lactones, lactides, and estolides. Particular attention is given to a description of Sulphan, a stabilised SO_3, which, provided it is kept away from atmospheric oxygen, is much more convenient to use. The sulphonation of

saturated aliphatic chain and ethylenic straight-chain compounds, and aromatic hydrocarbons, is especially considered. J. W. B.

Isomerisation of Aryl Sulphonates to Hydroxyaryl Sulphones. A. A. Aleykutty and V. Baliah. *J. Indian Chem. Soc.*, 31, 513–518 (July 1954).

Aryl benzenesulphonates and aryl p-toluenesulphonates isomerise when heated with anhydrous aluminium chloride to give mixtures of o- and p-hydroxyaryl sulphones. When the aryl group has a *para* substituent only the o-hydroxy-aryl sulphone is produced. A. J.
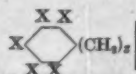
PATENTS

Detergents. Marchon Products. *BP* 723,916

Salts of sulphated ethylene oxide condensates whose hydrophobic portion is derived from a fatty alcohol, fatty acid, fatty amide, fatty alkylolamide, alkylphenol, alkylnaphthol or alkylphenylethyl alcohol, e.g. $C_{12}H_{25} \cdot O \cdot CH_2CH_2O \cdot SO_3Na$, have very good detergent properties for cotton fabrics. C. O. C.

Alkylene Polyamine Derivatives— Detergents and Wetting Agents having Metal-sequestering Properties. F. C. Bersworth. *BP* 721,196

Compounds of formula $ADN \cdot (CH_2)_n \cdot (ND \cdot (CH_2)_n) \cdot NDA$ (A = hydrocarbon of > 6 C or *cyclo*alkyl of 6 C in both cases being substituted by one or two $COOR^1$, COOM, OR^1 or OR^1OR^1 groups (R^1 = H or Alk; R^2 = alkylene; $D = CH_2 \cdot COOH$, $CH_2 \cdot COOM$, $CH_2 \cdot CH_2 \cdot COOH$, or $CH_2 \cdot CH_2 \cdot COOM$; M = alkali metal or ammonium) spaced at least 2 C atoms from the N atoms) are detergents compatible with soap and able to sequester metal ions. C. O. C.

Foaming Agents for Incorporation with Organic Ionic Soapless Detergents. Unilever. *BP* 723,212

Compounds of formula $R^1 \cdot (Ar)_n \cdot O \cdot R^2 \cdot CO \cdot NH \cdot R^3 \cdot OH$ (R^1 = straight or branched chain Alk, or acyl of 4–10 C including at least one straight chain of > 3 C when n = 1 or of 8–14 C including a straight chain of > 7 C when n = 0; Ar = phenylene or naphthylene; n = 0 or 1; R^2 and R^3 = alkylene, dialkylene ether or polyalkylene polyether radicals (alkylene of 1–4 C), $R^2 + R^3$ contain < 11 C), e.g. p-*tert.*-octylphenoxyacetethanol amide, added to organic ionic soapless detergents, give marked improvement in the stability of the lathers. C. O. C.

Surface Active Agents. General Mills. *USP* 2,668,851

Compounds of formula $R^1R^2N \cdot (C_nH_{2n}NR^2)_m R^3$ (R^1 = hydrocarbon of 8–22 C; R^3 = H or $CR^2_2SO_3M$ (R^2 = H or Alk; M = alkali metal or ammonium); n = 2–6; m = 1–6; at least one R^2 must be $CR^2_2SO_3M$) are wetting, emulsifying and detergent agents, e.g. $C_{12}H_{25}N(CH_2 \cdot SO_3Na)C_2H_6N(CH_2SO_3Na)_2$. C. O. C.

Iminazoline Lactates— Detergents for Use in Dry Cleaning Fluids. Alrose Chemical Co.

USP 2,669,546

The lactates of iminazolines substituted in the 2-position by a saturated aliphatic hydrocarbon of 17 C or in the 1-position by such groups as hydroxyethyl, aminoethyl, benzyl and ethyl benzene, are surface active agents which when incorporated in organic solvents produce unusually effective liquid detergents, in this respect being much superior to those mentioned by Brown (J.S.D.C., 49, 42 (1933)). C. O. C.

Conditioning and Lubricating Textiles. Atlas Powder Co. *USP* 2,668,785

Use of a scourable textile lubricant e.g. diethylene-glycolmonostearate or laurate, together with a compound of formula $ANR^1R^2R^3R^4$ (A = anion; R^1 = aliphatic hydrocarbon of 12–18 C; R^2 and R^3 = same or different, Alk, alkylol and aliphatic radicals and may form a ring with the N atom; R^4 = Alk or aralkyl), e.g. N-cetyl-N-ethyl morpholinium ethosulphate, impart softness, lubricity, ease of wetting and scouring, and antistatic properties to cellulosic textiles. C. O. C.

Sizing Nylon Yarns. Monsanto. *BP* 723,076

An aqueous solution at pH 2–5 and containing 2–15% by wt. of a water-soluble copolymer of 1 mol. of maleic acid, maleic anhydride or an alkyl half ester of maleic acid

(Alk of 1–4 C) with vinyl acetate is used to size nylon yarns for wearing. There should be 0·5–5·0% by wt. of the copolymer present on the dried yarns. The size is readily removed during scouring. C. O. C.

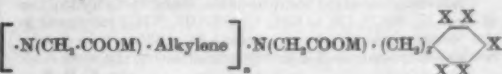### Starch Size Dispersible in Cold Water. Corn Products Refining Co. *USP* 2,669,523

Treating starch with an oxidising agent, gelatinising and dehydrating yields a product which is readily dispersible in cold water. Fabrics sized with the treated starch have no tendency towards spotting if they are sprinkled with water. C. O. C.

Substituted-aralkyl Polyalkylene Polyamine Polyacetic Acids— Metal-sequestering Bactericides and Fungicides. F. C. Bersworth. *BP* 721,640

Compounds of formula—

$$X\overset{X \quad X}{\underset{X \quad X}{\bigcirc}}(CH_2)_s\left[\cdot N(CH_2 \cdot COOM) \cdot Alkylene\right]_n \cdot N(CH_2COOM) \cdot (CH_2)_s\overset{X \quad X}{\underset{X \quad X}{\bigcirc}}X$$

(X = H, Alk, Hal, OH or alkoxy, 1–3 of the X group of each phenyl nucleus not being H; n = 1–4; s = 1–5; M = H, alkali metal, ammonium or substituted ammonium; Alkylene = ethylene, propylene or trimethylene) are water-soluble bactericides and fungicides having strong metal-sequestering power in both acid and alkaline solution. C. O. C.

Water-repellent Composition. S. C. Johnson & Son. *USP* 2,669,524

A solution containing (a) 1–10% by weight of petroleum wax and/or petrolatum and/or polymerised octadecyl vinyl ether, (b) 0·1–3·0% of zirconium ethoxide and (c) a mutual solvent for (a) and (b) confers optimum water-repellency to wool and when applied to cotton is resistant to dry cleaning. C. O. C.

Titanium and Antimony-containing Solutions for imparting a Flame-resistant Finish. DuP. *BP* 721,586

Certain monobasic acid solutions of Ti and Sb, especially their halides, are excellent agents even in relatively high dilution, for imparting a flame-resistant finish to cellulosic textiles which will meet all the requirements of the A.A.T.C.C. test. C. O. C.

Flameproofing Composition for Cellulosic Materials. DuP. *USP* 2,668,784

An aqueous acidic solution of Ti and tervalent Sb (Ti:Sb $\not>$ 10) by wt. and the atomic ratio of Sb:Ti $\not>$ 2) diluted with an aqueous solution of a volatile, initially stable organic liquid, e.g. isopropyl alcohol ($\not>$ 70% by wt. of organic liquid) is used to impregnate the material which is then neutralised and washed off. The flame- and glow-resistant finish obtained is fast to repeated washings. C. O. C.

Flame-resistant Composition for Incorporation in Thermoplastic Polymers. Diamond Alkali Co. *USP* 2,669,521

A mixture of a highly chlorinated organic material and an inorganic flame-retardant material is a useful flame-resistant composition for incorporation in natural or synthetic thermoplastic polymers. C. O. C.

Solvents and Plasticisers for Polyacrylonitrile. Eastman Kodak Co. *USP* 2,675,364

Phosphoryl morpholine, thionyl morpholine and thiophosphoryl morpholine are useful solvents and plasticisers for polyacrylonitrile. They can be used to make spinning solutions. C. O. C.

Tanning Agents. BASF. *BP* 722,370

Tanning agents having good exhaustion are produced by reacting dihydroxydiarylsulphones with sulphites and HCHO in the molecular proportion of 1:0·8–1·2:1–2. C. O. C.

Antioxidants. Monsanto. *USP* 2,670,382

Antioxidants specially suited for use with rubber consist of sulphides of 3:6-disubstituted phenols in which the substituents are linked to the nucleus through primary C atoms at least one substituent containing > 1 C atom, e.g. thio bis (3-methyl-6-benzylphenol). C. O. C.

Dry Cleaning (VII p. 199).

Cellulose Trisalkylcarbamates (XI p. 203).

Differences and Analogies in the Chemical Constitution of Syntans and Leather Dyes (XII p. 203).

Epoxyalkoxyaryl Resins— Coating Compositions, Fibres, Foils, etc. (XIII p. 204).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Reaction of Sulphonation. XXXIV— Hydrolysis of Sulphonic Acids of the Benzene Series. A. A. Sprýskov and N. A. Ovsyankina. *J. Gen. Chem. U.S.S.R.*, **24**, 1810–1814 (Oct. 1954).

Under sulphonation conditions the stability to hydrolysis of $X \cdot C_6H_4 \cdot SO_3H$ (X = OH, Cl, COOH, NH_2) increases in the order *ortho* < *para* < *meta*. At 163°c. *p*-hydroxybenzenesulphonic acid is slowly isomerised to the *meta* acid.
A. E. S.

Molecular Interaction and Colour. V— Absorption Spectra of Molecular Complexes of Nitro Compounds with Aromatic Amines. V. A. Izmail'skiĭ and A. N. Guseva. *J. Gen. Chem. U.S.S.R.*, **24**, 1402–1415 (Aug. 1954).

Investigation of the colour of molecular complexes of the type $A \cdot [K] \cdot H + H \cdot [K] \cdot B$ (for notation see J.S.D.C., **67**, 198 (1951); see also J.S.D.C., **68**, 464 (1952) and **69**, 506 (1953)) is continued. The complex formed by nitrobenzene and dimethylaniline (λ_{max} 310 mμ. and 315 mμ. respectively) is largely dissociated in dil. soln., but when a very large excess of nitrobenzene is present (i.e. as solvent) the absorption max. of the complex can be detected (429 mμ.; λ_{max} of $A \cdot [K] \cdot B$, i.e. $p \cdot NO_2 \cdot C_6H_4 \cdot N(CH_3)_2$, is 395 m$\mu$. in pyridine and 429 m$\mu$. in nitrobenzene). In a similar way, NN-dimethyl-p-anisidine and p-dimethylaminostilbene give complexes with nitrobenzene having absorption max. of ~ 430 mμ. The complexes between analogous cpd. containing longer conjugated systems are more stable. Thus for $K = -C_6H_4 \cdot CH : CH \cdot C_6H_4 \cdot$ (A and B as before) the complex can be detected in dil. pyridine soln. (λ_{max} when nitro cpd. is in excess in dilute soln., 438 mμ.; theoretical λ_{max} for no interaction, 355 mμ.; λ_{max} of $A \cdot [K] \cdot B$, 450 mμ.).
A. E. S.

Quinones. I— Sulphonation. A. P. Terent'ev and A. N. Grinev. *J. Gen. Chem. U.S.S.R.*, **24**, 1049–1058 (June 1954).

Full description, with experimental details, of work already reported briefly (see J.S.D.C., **68**, 317 (1952)). The extension of the method to the preparation of disulphonated trihydric phenols, e.g. 2:4:5-trihydroxybenzene-1:3-disulphonic acid, is described; 1:2-naphthaquinone yields a 1:2-naphthaquinonedisulphonic acid (orientation not established).
A. E. S.

Tautomeric Compounds. XVI— Mobility of Hydrogen Atoms in Condensation Products formed by 3-Methyl-1-phenylpyrazol-5-one with Ketones. XVII— Reaction of Diazo Compounds with the Condensation Products formed by 3-Methyl-1-phenylpyrazol-5-one with Ketones. A. E. Poraĭ-Koshits and M. S. Dinaburg. *J. Gen. Chem. U.S.S.R.*, **24**, 1221–1226 (July), 2208–2212 (Dec. 1954).

The condensation products (I: R^1 = CH_3, C_6H_5, and $m \cdot NO_2 \cdot C_6H_4$) formed by 3-methyl-1-phenylpyrazol-5-one with methyl ketones react in the cold with aldehydes ($R^2 \cdot$CHO: R^2 = phenyl and p-chloro-, 2:4-dichloro-, p-dimethylamino-, m-hydroxy-, 4-hydroxy-3-methoxy-, o-nitro-, and p-nitro-phenyl), and yield deeply coloured cpd. (II) (piperidine may be added as catalyst in some cases). The same condensation products react in the same position with diazonium salts (cf. J.S.D.C., **70**, 198 (May 1954) (Kharkharov)), but only in presence of mineral acid, so that salt-formation may occur in the 1-position. Ten azo dyes (III: R^3 = phenyl and m-carboxy-, 2:5-dichloro-, 4-chloro-2-nitro-, and p-nitro-phenyl) prepared in this way are described; they show considerable bathochromic shifts as compared with the corresponding dyes formed by coupling with 3-methyl-1-phenylpyrazol-5-one itself.

(I)

(II)
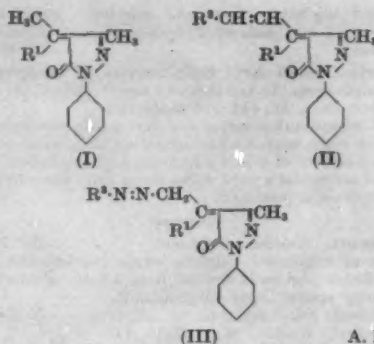
(III)   A. E. S.

Mechanism of the Formation of Benzimidazo[2,1-*a*]-benz[*de*]isoquinolin-7-one and its Amino Derivatives. B. M. Krasnovitskii and R. M. Matskevich. *J. Gen. Chem. U.S.S.R.*, **24**, 2027–2033 (Nov. 1954).

When a method developed for the preparation of m- and p-aminophenylimides of naphthalic acid is applied to the preparation of the *ortho* isomer (treatment of naphthalic anhydride with o-nitroaniline in presence of sodium hydrosulphite), only a small amount of the expected imide is obtained, the main product (formed from the imide by cyclisation) being benzimidazo[2,1-*a*]-benz[*de*]isoquinolin-7-one (I). Reduction of the nitro group precedes imide formation, for 2:4-dinitroaniline yields a mixture of 10- and 11-amino deriv. of I. The 11-amino deriv. is prepared also from naphthaloyl chloride by condensation with 2:4-dinitroaniline and reduction of the product. The amino deriv. are diazotised and coupled with 2-naphthol-3:6-disulphonic and 1:8-aminonaphthol-3:6-disulphonic acids, and yield acid dyes (colour not stated) giving dyeings on wool of good fastness to washing but poor fastness to perspiration.
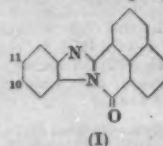

(I)   A. E. S.

Diazotisation of 2-Thienylamine and Preparation of Azo Compounds of the Thiophen Series. N. I. Putokhin and V. I. Yakovlev. *Dokladÿ Akad. Nauk S.S.S.R.*, **98**, 89–91 (1 Sept. 1954).

Difficulties arising from the instability of 2-thienylamine can be avoided by use of the stable, highly sol. double salt formed by its hydrochloride with stannic chloride, $SnCl_4, 2(C_4H_3S \cdot NH_2 \cdot HCl)$ (prepared by reduction of 2-nitrothiophen with tin in ethanol saturated with HCl). In this form the amine can be coupled with diazonium salts and can be diazotised and coupled with the usual components. The resulting dyes are similar in dyeing and other properties to the corresponding dyes of the benzene series— 15 monoazo (yellowish orange) and 7 disazo (red) dyes are prepared, typical examples being 1-(2-thienylazo)-2-naphthol, 1-(2-thienylazo)-2-naphthylamine, 1-(2-thienylazo)-2-naphthol-6:8-disulphonic acid, 5-phenylazo-2-thienylamine, 5-(2-thienylazo)-2-thienylamine, and disazo dyes formed by the further diazotisation and coupling of some of the monoazo dyes.   A. E. S.

Polysulphonamide Dyes. I— Preparation of Polysulphonamide Diazo Components. Y. P. Berkman and B. Y. Gordinskii. *Ukrain. Khim. Zhur.*, **18**, 168–178 (1952): *Chem. Abs.*, **48**, 13650 (25 Nov. 1954).

Aminosulphonic acids containing up to 6 benzene nuclei linked together by means of $SO_2 \cdot NH$ groups were prepared. Salt formation can be induced at the $SO_2 \cdot NH$ groups as well as in the sulpho groups. The products can be diazotised, although the diazo compounds with > 4 benzene nuclei are almost insoluble in water. Sodium sulphanilate condensed with m-nitrobenzenesulphonyl chloride in presence of chalk to give the Ca salt of—

O₂N⟨⟩SO₂·NH⟨⟩SO₃H
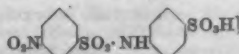
Reduction with ammonium sulphide gave the corresponding NH₂ compound, which condensed with additional *m*-nitrobenzenesulphonyl chloride to give—

O₂N⟨⟩SO₂·NH⟨⟩SO₂·NH⟨⟩SO₃H
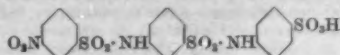
Similar alternate reduction and condensation reactions were carried out until 6 benzene nuclei had been linked together. The amino compounds diazotise slowly, and couple to give azo dyes in the usual manner.   E. S.

Disperse Monoazo Dyes containing an N-3-Oxobutyl Group. N. Kuroki and K. Konishi. *Bull. Naniwa Univ.*, **2A**, 135–140 (1954): *Chem. Abs.*, **48**, 14212 (25 Nov. 1954).
N-Ethyl-*N*-3-oxobutylaniline, prepared by adding CH₃·CO·CH:CH₂ to *N*-ethylaniline at 35°c. and stirring at 20–25°c. for 93 hr., was coupled with various diazo compounds to give disperse dyes for cellulose acetate, nylon, and Vinylon. Diazotised *p*-nitroaniline, for instance, gave a light brown.   E. S.

Ethyleneazo Dyes of the Quinoline Series. M. Seyhan. *Chem. Ber.*, **86**, 572–574 (1953): *Chem. Abs.*, **48**, 14213 (25 Nov. 1954).
Lepidine was heated with SeO₂ in *m*-xylene at 135–140°c. to give 4-quinolinecarboxaldehyde, which was condensed with *p*-nitro- and 2:4-dinitro-phenylhydrazine to give the corresponding hydrazones. These were heated with alcoholic ethyl iodide to give the quaternary ethyl iodides, converted by treatment with conc. KOH into azo compounds; e.g. the *p*-nitrophenylhydrazone gave 4-*p*-nitrophenylazomethylene-1-ethyldihydroquinoline.   E. S.

Effect of High-energy Radiation on Azo Dyes. Ultramid Foils. H. Hinrichs. *Z. physikal. Chem.* [N.F.] (Frankfurt), **2**, 40–51 (1954): *Chem. Abs.*, **49**, 62 (10 Jan. 1955).
In foils of Ultramid 1 C (BASF), in which the fluorescence had been extinguished by incorporating the red dye phenylazophenyl-2-naphthylamine, a fluorescence much stronger than that characteristic of Ultramid 1 C was observed under cathode-ray excitation. Whether the αβ-naphtho-2:3-diphenyl-1:2:3-triazolium ion is formed is uncertain. Diagrams show the fluorescence extinction as wavelength function and the shifting of spectral lines. The possible mechanism of the reaction caused by irradiation is discussed.   C. O. C.

The Infrared Spectra of Some Unsulphonated Monoazo Dyes. M. Dolinsky and J. H. Jones. *J. Assocn. Off. Agric. Chem.*, **37**, 197–209 (1954): *Chem. Abs.*, **49**, 58 (10 Jan. 1955).
The infrared spectra of some unsulphonated azo dyes and related compounds are given. Absence of characteristic infrared peaks in the 3-μ and 6-μ regions seems to support the zwitterion type of structure for the *o*-hydroxyazo compounds and not a hydroxyazo–benzoquinone hydrazone tautomer. The nature of the infrared absorption in the 3-μ and 11–15-μ regions may be of value in establishing the position and the nature of substituents in the azo dye molecule; furthermore, each unsulphonated monoazo dye has a unique infrared absorption spectrum. The characteristic band in the 7-μ region assigned to the azo groups seems to be too weak to be of practical value in characterising aromatic azo compounds. 31 figures.   C. O. C.

Effect of Spatial Structure on the Colour of Benzidine Disazo Dyes. B. M. Krasovitskiĭ and D. G. Pereyaslova. *Dokladȳ Akad. Nauk S.S.S.R.*, **98**, 71–74 (1 Sept. 1954).
Benzidine and its deriv. are tetrazotised and coupled with H acid, and the absorption spectra of the resulting dyes are determined in aq. soln. and as dyeings on Cellophane. The value of λ_max is frequently much higher for the dyeing than for the soln. It is considered that in these cases the diphenyl rings are inclined at an angle in the soln., and pass into a more closely linear and coplanar state, with consequent increase in the conjugation of the

system, when the molecule is adsorbed on cellulose. In some of these cases (2- and 2:2′-deriv. in which steric hindrance occurs), conjugation between the two diphenyl rings is so low that λ_max for the soln. approaches the value for the monoazo dye from the corresponding benzene deriv., but the forces that come into play when dyeing occurs are largely able to overcome these steric effects, and a considerable rise in λ_max occurs. For other 2:2′-deriv., however, λ_max is low both in soln. and on the cellulose. The results obtained are as follows—

Substituents	λ_max of Soln. (mμ.)	λ_max of Film (mμ.)
Nil	580	595
3:3′-di-CH₃	580	620
3:3′-di-OCH₃	595	640
3:3′-di-COOH	575	605
3:3′-di-NO₂	560	570
3:3′-di-Cl	580	580
2:2′-di-CH₃	550	565
2:2′-di-OH	550	600
2:2′-di-OCH₃	555	585
2:2′-di-COOH	560	570
2:2′-di-NO₂	535	550
2:2′-di-F	555	585
2:2′-di-Cl	550	560
2:2′-di-Br	550	565
2-CH₃	560	605
2-NO₂	560	585
2-I	550	590

A. E. S.

Scission of Carbon–Carbon Bonds by Diazo Compounds. I— Reaction of Tertiary Amines of the Triphenylmethane Series with Diazo Compounds. V. V. Perekalin and L. P. Popova. **II— Reaction of Tertiary Amines of the Diphenylmethane Series and Dimethylaniline Derivatives with Diazo Compounds.** V. V. Perekalin, L. P. Popova, and T. I. Abramovich. *J. Gen. Chem. U.S.S.R.*, **24**, 1226–1232, 1233–1238 (July 1954).
Many cpd. in which the *p*-dimethylaminoaryl group is attached to carbon will react with active diazonium salts (e.g. *p*-nitrobenzenediazonium chloride) with scission at the point of attachment and formation of a *p*-arylazodimethylaniline. A typical example is the reaction of the leuco base of Crystal Violet (not given by the dye itself)— the leuco base (1 mole) with 2 moles of diazonium salt yields 2 moles of the azo dye and 1 mole of *p*-dimethylaminobenzaldehyde (which can itself undergo this reaction); with 3 moles of diazonium salt it yields 3 moles of the azo dye and 1 mole of formic acid. Among other substances giving analogous reactions are leuco Malachite Green, Michler's ketone and hydrol, and *p*-dimethylaminobenzyl alcohol.   A. E. S.

Structures and π-Electron Spectra. II— The Transformation Matrix. W. T. Simpson and C. W. Looney. *J. Amer. Chem. Soc.*, **76**, 6285–6292 (20 Dec. 1954). **III— Triphenylmethane Dyes.** C. W. Looney and W. T. Simpson. *Ibid.*, 6293–6300.
II— A definite procedure is given for constructing a transformation matrix relating π-electron spectra to structures. Arbitrariness in the transformation matrix which may exist even after the incorporation of symmetry is discussed, and a method of removing it is shown in the cases of Crystal Violet and *p*-methoxy Malachite Green.
III— The positions, intensities, and symmetry classifications of the visible and near ultraviolet bands are given for Crystal Violet, *p*-methoxyMalachite Green, Malachite Green, *p*-nitroMalachite Green, and Michler's hydrol blue. The observed transition energies and polarisations for Crystal Violet and methoxyMalachite Green were used in II as the data for a theoretical treatment using the methods of the structure representation. The observed intensities for Crystal Violet are here similarly used. Using only these data transition energies for Malachite Green and intensities for methoxyMalachite Green and Malachite Green are calculated theoretically and compared with experiment. Electric moments of the structures are worked out. The transition energies and intensities of *p*-nitroMalachite Green and Michler's hydrol blue are also treated theoretically. Finally a set of relative basicities are deduced from the spectral data, spectroscopic resonance energies calculated, and heats of carbinol formation predicted.   C. O. C.

Unsymmetrical Dithizone Analogues. L. S. Pupko and P. S. Pel'kis. *J. Gen. Chem. U.S.S.R.*, **24**, 1640–1645 (Sept. 1954).

Unsymmetrical dithizone analogues, $C_6H_5 \cdot NH \cdot NH \cdot CS \cdot N:N \cdot Ar$ (Ar = o-, m-, and p-tolyl, o- and p-methoxyphenyl, o-phenoxyphenyl, 2:4-dibromophenyl), are prepared by coupling, successively, the two appropriate diazonium salts with nitromethane, and treating the product first with ammonium sulphide (formation of $C_6H_5 \cdot NH \cdot NH \cdot C(SH)(NH_2) \cdot NH \cdot NH \cdot Ar$), and then with alcoholic alkali (loss of ammonia and oxidation). Except in the case of the dibromo cpd., the two absorption max. in the visible region are moved towards the longer waves by amounts ranging up to 40 mμ. (as compared with dithizone itself), and the long-wave max. is very close to the arithmetic mean of the values for the two corresponding symmetrical cpd. All give complex cpd. with Pb, Hg, Zn, and Ag, and the absorption max. of these are again higher than those of the corresponding dithizone cpd.   A. E. S.

Organic isoCyanates. IV— Reactions of Phenyl and 1-Naphthyl isoThiocyanates in presence of Aluminium Chloride. N. S. Dokunikhin and L. A. Gaeva. *J. Gen. Chem. U.S.S.R.*, **24**, 1871–1873 (Oct. 1954).

The authors have previously shown that 1-naphthyl isocyanate yields naphthostyril when fused with $AlCl_3$ and NaCl. Under similar conditions 1-naphthyl isothiocyanate gives thionaphthostyril, readily converted into naphthostyril by treatment with acids.   A. E. S.

Synthesis of Thiazolostyryl Cyanine Dyes. J. C. Banerji and K. Banerjee. *J. Indian Chem. Soc.*, **31**, 509–512 (July 1954).

Four new cyanine dyes (I: X = CH_3, Cl, Br, I) have been prepared by condensing p-dimethylaminobenzaldehyde with 4-p-tolyl-, 4-p-chlorophenyl-, 4-p-bromophenyl-, and 4-p-iodophenyl-2-methylthiazole in absolute ethanol in the presence of piperidine and subsequently heating the bases with methyl iodide. The dyes are soluble in alcohols but insol. in water, ether, or benzene. All four dyes produce extrasensitisation of a photographic plate up to ca. 6250 A. There is a progressive shift in the wavelength of max. sensitisation with increasing mol. wt. for the first three dyes. The fourth is the poorest extrasensitiser, producing an effect similar to the unsubstituted dye (I: X = H).
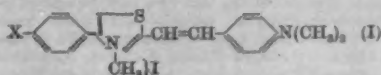
A. J.

Cyanine Dyes. IX— Some Tetramethoxythiacarbo-cyanines. I. I. Levkoev, Z. P. Sýtnik, S. V. Natanson, V. V. Durmashkina, T. V. Krasnova, and R. S. Shuser. *J. Gen. Chem. U.S.S.R.*, **24**, 2034–2039 (Nov. 1954).

The synthesis and properties are described of 16 symmetrical tetramethoxythiacarbocyanines of formula—
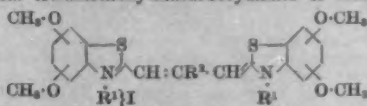
(R^1 = CH_3 or C_2H_5; R^2 = H, CH_3, or C_2H_5), 4:5:4′:5′-, 4:6:4′:6′-, 4:7:4′:7′-, and 5:6:5′:6′-tetramethoxy cpd. being represented (cf. J.S.D.C., **68**, 467 (1952)). Introduction of an extra pair of methoxyl groups into a symmetrical dimethoxythiacarbocyanine causes a bathochromic change, except when a 4:5:4′:5′-tetramethoxy cpd. results; in this case λ_{max} lies between the λ_{max} values for the 4:4′- and 5:5′-dimethoxy cpd., a fact that is to be associated with steric hindrance effects, it being impossible for the methoxyl groups to be coplanar with the radical on the nitrogen.   A. E. S.

Amino Derivatives of Thiacyanine Dyes— V and VI. E. D. Sych. *Ukrain. Khim. Zhur.*, **18**, 148–158 (1952): *Chem. Abs.*, **48**, 13683 (25 Nov. 1954).

Various derivatives of 2-methylbenzothiazoles were converted into thiacarbocyanines and to trimethincyanine iodides. It was shown that Cl in ortho position to an NO_2, NH_2, or Acyl·NH group in thiacarbocyanines having two polar groups in each ring has little effect on the light absorption; dyes in which NH_2 and NO_2 are both present show the most intense colour. Thus, nitration of 5-chloro-2-methylbenzothiazole gave mainly the 6-nitro derivative. Reduction of the NO_2 group with Sn and HCl, followed by methylation with methyl p-toluenesulphonate, gave the 6-dimethylamino compound. This product heated with ethyl p-toluenesulphonate gave a quaternary salt which in pyridine with triethyl orthoformate and acetic anhydride gave the thiacarbocyanine. The quaternary ethiodide of 5-chloro-2-methyl-6-nitrobenzothiazole heated with triethyl orthoformate in pyridine gave bis-(5-chloro-3-ethyl-6-nitro-2-benzothiazole)trimethincyanine iodide (absorption max. 578 mμ.), which with Sn, HCl, and acetic acid gave the bis-6-amino compound.   E. S.

Synthesis of Benzanthrone and Dyes derived from it. II— Synthesis of isoDibenzopyrenequinone from Benzanthrone. E. Koike, I. Tanakadate, and T. Kaneko. *J. Chem. Soc. Japan*, Ind. Chem. Sectn., **55**, 478–481 (1952): *Chem. Abs.*, **49**, 265 (10 Jan. 1955).

Alkaline condensation of benzanthrone and $C_6H_5 \cdot CH_2 \cdot CN$ in presence of pyridine at 60°c. yields 80·8% α-phenyl-7-oxo-7H-benz[de]anthracene-4-acetonitrile. It is necessary for C_2H_5OH to be present as well as pyridine. The important factor influencing the reaction is the ratio pyridine : C_2H_5OH : KOH. $K_2Cr_2O_7$ oxidation of the condensate yielded 96·7% 4-benzoyl-7H-benz[de]anthracene-7-one, which when fused with a mixture of $AlCl_3$ and NaCl (7 : 1 by wt.) yielded 93% of the red vat dye dibenzo-[a,i]pyrene-5:8-dione.   C. O. C.

Preparation of 5-Iodo-3-hydroxythionaphthen and its Condensation with Isatin and its Derivatives. A. K. Sinha. *J. Indian Chem. Soc.*, **31**, 463–466 (June 1954).

5-Iodo-3-hydroxythionaphthen, obtained from 4-iodo-2-carboxyphenylthioglycollic acid, has been condensed with isatin and its 5-chloro, 5-bromo, 5:7-dibromo, 5-bromo-7-nitro, and 5:7-dinitro derivatives to give thioindigoid dyes of general formula I. These violet–red dyes, which gave yellowish-green to green solutions in conc. sulphuric acid, dyed cotton various reds from yellow vats, and dyed wool from a dilute sulphuric acid dyebath.

Oxidation of 5-iodo-3-hydroxythionaphthen gave 5:5′-di-iodothioindigo, which was reduced at 85–90°c. to give a deep yellow vat, from which cotton was dyed pink.
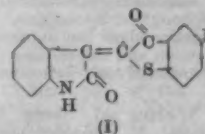
(I)   C. H. R.

Some Dehydrogenation Products of α-Carotene, β-Carotene, and Cryptoxanthin. G. Karmakar and L. Zechmeister. *J. Amer. Chem. Soc.*, **77**, 55–60 (5 Jan. 1955).

Treatment of α-carotene, β-carotene, and cryptoxanthin with N-bromosuccinimide and (in part) with N-bromoacetamide yielded the more deeply coloured dehydro-β-carotene, bisdehydro-β-carotene, and anhydro-escholtzxanthin and in addition three intensely coloured orange-yellow crystalline pigments, dehydrocarotenes I–III. Dehydrocarotene I was obtained only from α-carotene, II from β-carotene, and III from both carotenes. Their spectral curves are characterised by lack of fine structure in the visible region. When dehydrocarotenes I and II are treated with boron trifluoride etherate, dark blue complexes quickly form, and these when cautiously hydrolysed yield hydrocarbons whose visible spectra again show the fine structure of that of carotene. This can be explained simply by a migration of the double bond formed during dehydrogenation, out of conjugation from the main chromophore, i.e. by the rearrangement 3:4-dehydro compound → 2:3-dehydro compound. This is similar to the behaviour of desoxylutein I, $C_{40}H_{56}O$ (prepared by melting lutein with naphthalene and anhydrous boric acid), which also forms a complex with boron trifluoride, the product obtained by cleavage of this complex having a spectral curve with a fine structure.   C. O. C.

Study of the Chinese Yellow Drug— Isolation of Two Yellow Dyes, Rhamnus Yellow A and B. Jen-Hung Chu. *Ko-Hsueh T'ung-Pao* (Scientific News), **1**, 458 (1950): *Chem. Abs.*, **49**, 191 (10 Jan. 1955).

Two yellow dyes, Rhamnus Yellow A and B, have been isolated from the Yellow Drug (called after its colour) *Rhamnus Crenata*. They have empirical formulae $C_{15}H_{20}O_6$ and $C_{13}H_{16}O_4$ respectively, and some of their properties are given.   C. O. C.

PATENTS

**Acetoacetylamino Compounds.** DH.   *BP 723,057*

Certain amines, e.g. aminoanthraquinones, secondary diarylamines, some anilinesulphonamides, and heterocyclic compounds having a secondary N atom in the nucleus, which do not react readily with diketene under aqueous conditions to give *N*-acetoacetyl compounds, react smoothly if the process is carried out in 90–100% acetic acid at 40–80°c.   E. S.

Aliphatic Azo Compounds— Polymerisation Catalysts. DuP.   *USP 2,666,758*

Aliphatic azo compounds

$$R^1OCH_2 \cdot C(CN)(R^3) \cdot N:N \cdot C(CN)(R^3) \cdot CH_2 \cdot OR^4$$
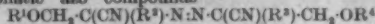
(R^1 and $R^4 =$ Alk of < 5 C; R^2 and $R^3 =$ Alk preferably of < 5 C) are prepared by the following steps— (a) treatment of a suitable ketone with hydrazine to form the azine, (b) treatment of the azine with HCN, (c) oxidation of the resulting hydrazonitrile with Cl or Br to give the azonitrile. Thus methoxyacetonitrile is treated with CH_3MgBr to give methoxyacetone, which is condensed with hydrazine hydrate. Treatment with HCN and then with chlorine gas gives $\alpha\alpha^1$-azobis-α-methyl-β-methoxypropionitrile—
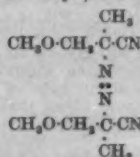
The products are polymerisation catalysts, particularly for compounds having a CH_2:C group, e.g. vinyl compounds.   E. S.

2-Substituted Indazolones as Colour Couplers. ICI.   *BP 722,281*

Compounds of formula—
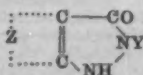
($Z =$ atoms to complete an isocyclic, heterocyclic or polycyclic nucleus; $Y = COR^1$, $COOR^1$, SO_2R^1, $CONHR^1$, $CONR^1R^2$ or $CSNHR^1$ (R^1 and $R^2 =$ subst. or unsubst. hydrocarbon)) are used as colour couplers in colour photography where a primary aromatic amino developer is used. They are more resistant to oxidation than known indazolone colour couplers and do not yield yellow oxidation products in the silver bleaching bath. C. O. C.

**Yellow and Orange Monoazo Disperse Dyes.** S.   *BP 722,474*

Monoazo dyes
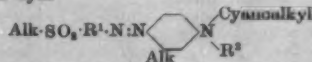
($R^1 =$ benzene or naphthalene residue which may contain $Alk \cdot SO_2$-, Alk, fluoroalkyl, or Hal substituents; $R^2 =$ Alk or hydroxyalkyl) give yellows and oranges on acetate and nylon. Thus 2-chloroaniline-4-methylsulphone is diazotised in conc. H_2SO_4 by adding $NaNO_2$ and drowning in ice and water, and coupled with *N*-cyanoethyl-*N*-hydroxyethylaniline, to give an orange yellow.   E. S.

Dischargeable Orange Disazo Direct Cotton Dyes. General Aniline.   *USP 2,666,757*

Phosgenation of monoazo dyes 2-naphthylamine-disulphonic acid → p-cresidine gives dischargeable orange direct cotton dyes of good acetate reserve properties. Their light fastness on viscose rayon is not impaired by a crease-resisting finish. Thus the monoazo dye 2-naphthyl-amine-4:8-disulphonic acid → p-cresidine is treated with phosgene at 20–95°c. whilst maintaining pH 7–8 by additions of aq. NaOH, to give the bright orange disazo dye.
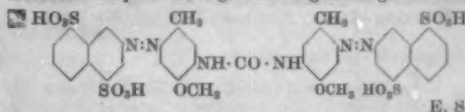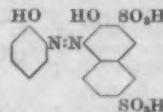
Metal(Copper)-complex Disazo Direct Cotton Blue. General Aniline.   *USP 2,667,476*

The copper complexes of the disazo dyes, a 3-methyl pyrazolone ← dianisidine → naphtholdisulphonic acid, are reddish blue direct cotton dyes of good resistance to synthetic resin finishes. Thus tetrazotised dianisidine is coupled first with 1 mol. of R salt in presence of $NaHCO_3$ and then with 1 mol. of 3-methyl-1-*m*-sulphophenyl-5-pyrazolone. The copper complex of the resulting disazo compound is made by heating at 85°c. with ammoniacal copper sulphate.   E. S.

**Metal(Chromium)-complex *oo'*-Dihydroxyazo Dyes.** Cincinnati Chemical Works.   *USP 2,668,167*

o-Alkoxy-*o'*-hydroxyazo compounds may be conveniently converted into the chromium complexes of the corresponding *oo'*-dihydroxyazo compounds by first reacting with copper salts, and then reacting the copper complex of the *oo'*-dihydroxyazo compound so formed with chromium salts under acid conditions. Thus the monoazo compound *o*-anisidine → R acid is coppered, and then refluxed for 20–30 hr. with a soln. prepared from Cr_2O_3, H_2SO_4, and sodium formate, to give the chromium complex of the *oo'*-dihydroxyazo compound.   E. S.

Direct Cotton Trisazo Blacks for Aftercoppering. S.   *BP 722,477*

Trisazo compounds—
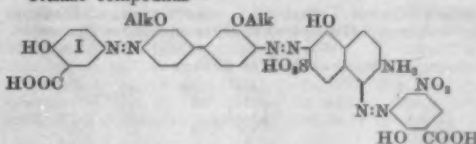
(I may contain further substituents) dye cellulose fibres dull violet, converted to black by aftercoppering. Thus dianisidine is tetrazotised and coupled, first with an alkaline soln. of 1 mol. of salicylic acid and then, preferably in the presence of 5–10% crude pyridine bases, with 1 mol. of the monoazo compound obtained by acid coupling of diazotised 3-amino-5-nitrosalicylic acid with J acid.   E. S.

Green and Olive Metal(Copper)-complex Trisazo Direct Cotton Dyes. S.   *BP 722,949*

The copper complexes of trisazo dyes
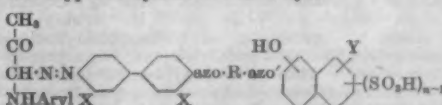
($R =$ aryl containing *ortho* to the azo' group a group capable of forming a metal complex; one $X =$ H, the other $X = SO_3H$; $Y =$ H or an amino group which may be alkylated, arylated or acylated; $n = 1$, 2 or 3; OH is *ortho*, and azo is *para*, to azo') are green to olive dyes for cotton. Thus benzidine-3-sulphonic acid is tetrazotised and coupled with one mol. of acetoacetanilide dissolved in aq. NaOH, and then with one mol. of 2-methoxy-1-naphthylamine-6-sulphonic acid. The amino disazo dye so formed is diazotised and coupled with *N*-phenyl-J acid in presence of pyridine, and the copper complex of

the resulting trisazo dye is made by refluxing it with ammoniacal copper sulphate. The product dyes cellulose bright green.   E. S.

Fluorescent Brightening Agent for Use in Laundry Marking Inks. National Marking Machine Co.   *BP 723,357*

Compounds of formula—

$$\left[=CH\bigcirc NH\cdot(\cdot CO\cdot\bigcirc NH)_n\text{-}X \right]_2$$
$$SO_3Na$$
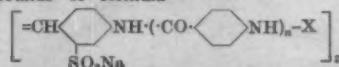
(X = aromatic acyl; $n = > 2$), e.g. 4:4′-di-p-(benzoyl-aminobenzoylaminobenzoylamino)-stilbene-2:2′-disodium sulphonate, fluoresce white under ultraviolet radiation and can be used as the marking agent in colourless marking inks.   C. O. C.

Fluorescent Brightening Agents. S.   *BP 723,288*
4-Methyl-7-diethylamino coumarin or a salt thereof is mixed with several times its weight of a solid, acid, water-soluble compound derived from a strong inorganic acid, e.g. sodium bisulphite or urea nitrate to yield a fluorescent brightening agent which readily dissolves in 5–10 parts of cold water to yield a clear solution which remains clear on dilution to normal working strengths, i.e. 25 mg./l.   C. O. C.

1:4-Diaminoanthraquinone-2:3-dicarboximides—Disperse Dyes for Polyethylene Terephthalate. DuP.   *BP 723,079*
1:4-Diaminoanthraquinone-2:3-dicarboximide, made by heating in H_2SO_4, either the 2:3-dicarbamyl or the 2:3-dicyano derivative is converted to the corresponding alkylimides which are green-blue light-fast dyes for polyethylene terephthalate materials. Thus the dye—
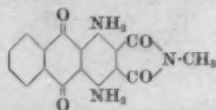
is prepared by heating 1:4-diaminoanthraquinone-2:3-dicarboximide in a mixture of methanol and o-dichloro-benzene containing methylamine under pressure at 175–180°C. for 4 hr.   R. K. F.

Anthraquinone–Triazines containing Methyl-sulphonyl Groups—Vat Dyes. American Cyanamid.   *USP 2,650,920*

Orange to red vat dyes of formula—

(R = H or Alk)
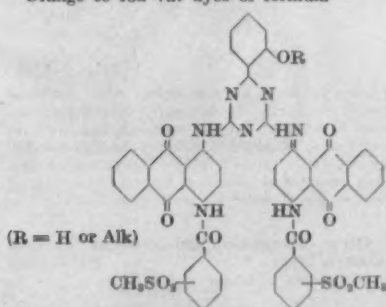
are made by condensing an o-alkoxyphenyldichloro-triazine with a 1-amino-4-(methylsulphonylbenzoylamino)-anthraquinone. Thus o-methoxyphenyldichlorotriazine and 1-amino-4-(m-methylsulphonylbenzoylamino)anthra-quinone are heated together in nitrobenzene at 150°C.   R. K. F.

Leuco-anthraquinone-acridone Sulphuric Esters. American Cyanamid Co.   *USP 2,649,452*
1-Arylamino-2-carboxyanthraquinones are treated with a metal e.g. Zn, Fe or Cd, in presence of the SO_3 addition product of a tertiary amine. Cyclisation proceeds simultaneously with esterification to give the corresponding *leuco*-anthraquinone-acridone sulphuric esters. Thus Zn is added to a suspension of 1-(β-naphthylamino)-2-carboxyanthraquinone in chlorobenzene containing tri-methylamine and $ClSO_3H$ at 50°C. Separation is effected

by pouring into aq. NaOH and distilling to remove chloro-benzene and the excess amine.   *USP 2,649,453*
Similar products are obtained by carrying out the reactions in aq. alkali, $Na_2S_2O_4$ replacing the metal.   R. K. F.

1 : 5 - Dihydroxy - 8 - nitro - 4 - phenylaminoanthra-quinones—Disperse Dyes. Eastman Kodak.   *BP 722,367*
1:5-Dihydroxy-4:8-dinitroanthraquinone is condensed with an amine—

$$X\bigcirc Y$$
$$NH_2$$

(X = monohydroxyalkyl of 1–3 C; dihydroxyalkyl of 2–3 C; or –$(OC_2H_4)_n$·OR, where $n = 1$–4 and R = H or Alk of 1–2C. Y = H, Cl, OH, OCH_3 or CH_3) to give blue disperse dyes with good light and burnt gas fume fastnesses. Thus 1:5-dihydroxy-4:8-dinitroanthraquinone and o-aminophenylethyl alcohol are refluxed in n-amyl alcohol for 7 hr. to give the dye—
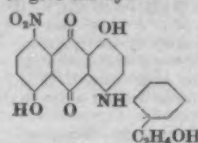
        R. K. F.

Sulphur-containing Vat Dyes. CFM.   *BP 722,575*
The vat dyes of *BP 299,972* (J.S.D.C., **45**, 89 (March 1929)) which are obtained by heating the reaction products of an anthrone and glyoxal in an alkaline melt, are treated with a S-containing compound e.g. a sulphur halide, an alkali metal sulphide or thiosulphate, in an acidic condensing agent other than a trivalent metal halide, e.g. H_2SO_4 or $ClSO_3H$. Thus, the violet dye obtained from the 2-chloroanthrone-glyoxal reaction product of *BP 299,972* is added to a mixture of H_2SO_4 and sulphur chloride and heated at 70–80°C. for 1·5 hr. There results an olive vat dye.   R. K. F.

Thionaphthene - benzanthrone — Vat Dye. General Aniline.   *USP 2,648,676*
Benzanthrone-3-carbonyl chloride and thionaphthene are heated together in presence of $AlCl_3$ at 75–80°C. for 3 hr. in nitrobenzene. After separating, the product is cyclised in molten $AlCl_3$-NaCl at 160°C. while passing a stream of oxygen through for 45 min. The resulting compound—
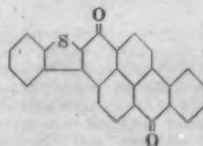
after isolating by pouring into aq. HCl, is an orange vat dye fast to chlorine.   R. K. F.

Methylated Pyrazole-anthrone-benzanthrones—Vat Dyes. General Aniline.   *USP 2,647,899*
The pyrazole-anthrone-benzanthrone Indanthrene Navy Blue R is chloromethylated by treating with dichloro-dimethyl ether in H_2SO_4, to produce a dye faster to water spotting than the original dye. Alternatively 9-chloro-methyl-4-bromobenzanthrone is condensed with pyrazole-anthrone. The chloromethyl groups are converted to CH_3 by vatting. Thus Indanthrene Navy Blue R is treated with dichlorodimethyl ether in H_2SO_4 at 60°C. for 15 hr., and the resulting compound vatted and isolated by oxidising with air.   R. K. F.
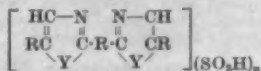
Fluorescent Brightening Agents. LBH.   *BP 722,791*
Compounds of formula—

$$H_3C\text{-}C\overset{C\text{-}HR^2}{\underset{C\text{-}CH_3}{\overset{||}{\underset{N}{\underset{H}{}}}}}R^2C\overset{CR^1}{}$$
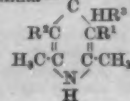
(R^1 and R^2 = carbalkoxy, carbaralkoxy, N-phenyl-carbamido or N-(subst. phenyl)-carbamido; R^3 = CH$_3$, C$_2$H$_5$ or Ar), e.g. 2:4:6-trimethyl-1:4-dihydropyridine-3:5-dicarboxylic acid methyl ethyl ester, are particularly effective fluorescent brightening agents for application to wool, other animal fibres and nylon. They also have affinity for cellulose acetate and to a lesser extent for cellulose. They are used as aqueous dispersions or solutions.   C. O. C.

Heterocyclic Fluorescent Brightening Agents. CFM.
BP 722,543

Compounds of formula—

$$\begin{bmatrix} HC\text{—}N & N\text{—}CH \\ RC & C\cdot R\cdot C & CR \\ Y & Y \end{bmatrix}(SO_3H)_n$$

(R = Ar or Ar-vinyl; Y = O or S; n = 1, 2 or 3) e.g. sulphonated 1:4-di(5′-phenyloxazolyl-2′)benzene, are good fluorescent brightening agents showing a blue fluorescence.   C. O. C.

Victoria Pure Blue BOC. DuP.   *USP* 2,668,172
Victoria Pure Blue BOC, i.e. [tetraethyl-diamino-diphenylethyl-α-amino naphthyl methane] [HCl] 1·00-1·10, is obtained in a form which does not tend to crystallise or form a sludge in hot castor oil and so is very suitable for carbon paper manufacture, by incorporating with it as stabilising agent 4-20% (on the dry wt. of dye) of the Na salt of dibutyl-o-phenylphenoldisulphonic acid.
C. O. C.

Stable, Concentrated Aqueous Solutions of Sulphur Dyes. Southern Dyestuff Corpn.   *BP* 721,333
Very strong aqueous solutions of leuco sulphur dyes are obtained by use of a little of a hydrotropic agent when making the solution. Suitable agents are p-toluene sodium sulphonate, tetrahydronaphthalene sodium sulphonate and xylene sodium sulphonate. Their use enables a lower pH and a stronger dye liquor to be used without causing precipitation or formation of tar. In addition the solid dyes are more soluble in presence of these agents and more reducing agent can be used.   C. O. C.

Metal Phthalocyanines. General Aniline.
USP 2,647,127
The yield of metal phthalocyanine obtained in the "urea-solvent" process is increased by having present < 25% of an aliphatic monobasic sulphonic acid containing 1–5C, or a salt or ester of one, or a derived amide or acid halide. Thus phthalic anhydride, urea, ammonium molybdate, ethane sulphonic acid and AlCl$_3$ are refluxed in trichlorobenzene for 11 hr. An 85% yield of chloro-aluminium phthalocyanine is obtained.

USP 2,647,128
The aliphatic sulphonic acid is replaced by an alkali metal, alkaline earth or NH$_4$ salt of a phosphoric acid. Thus in the above example, NaH$_2$PO$_4$ replaces ethane sulphonic acid to give a similar result.   R. K. F.
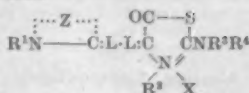
Tetracyano- and tetracarboxy-phthalocyanines. General Aniline.   *USP* 2,647,908
Dihalogenocyano-benzenes and -naphthalenes in which at least two of the substituents are o to one another, are fused with cuprous cyanide to produce tetracyano-phthalocyanines which are hydrolysed to give water soluble tetracarboxyphthalocyanines useful for colouring inks, wallpaper etc. Thus, a mixture of 2-cyano-3:5-dichlorodiphenyl and 2:5-dichlorobenzonitrile is heated at 275–290°c. for 3 hr. with cuprous cyanide. The product is hydrolysed by treating at 100–105°c. for 4 hr. with 90% H$_2$SO$_4$.   R. K. F.

Finely-divided Phthalocyanine Pigments. American Cyanamid Co.   *USP* 2,669,569
Use of extremely finely-divided solid grinding aids having a surface area > twice that of the particles previously used considerably shortens the grinding time needed to develop the ultimate pigment strength. For equal times of grinding in the same suspending liquor, the finer the degree of subdivision of the solid grinding aid the greater the tinting strength, brightness and depth of mass tone of the finished phthalocyanine pigment.   C. O. C.

Polymethin Dyes. Kodak.   *BP* 721,854
Dyes of formula—

$$\begin{array}{c} \cdots Z \cdots \quad OC\text{--}S \\ R^1N\text{——}C{:}L{\cdot}L{:}C \quad CNR^3R^4 \\ N \\ R^2 \quad X \end{array}$$

(R^1 and R^3 = same or different, subst. or unsubst. Alk; R^3 and R^4 = same or different, Alk or Ar or together = atoms to complete a 6-membered ring with the N atom; L = subst. or unsubst. methin; X = anion; Z = atoms to complete a thiazole, thiazoline, oxazole or selenazole nucleus or its benz-derivative) are photographic sensitisers.
C. O. C.

Barium Sulphate. Usines Chimiques des Laboratoires Français Uclaf.   *BP* 724,272
BaSO$_4$ readily reducible to a fine powder which gives stable aqueous suspensions by simple mixing with water is obtained by precipitating a solution of BaCl$_2$ with Na$_2$SO$_4$, washing the precipitate to yield a paste containing 25–35% by weight of water, mixing the paste with sodium citrate and drying at a moderate temperature. C. O. C.

Recovering Carbon Black from Gaseous Suspension. Columbian Carbon Co.   *USP* 2,668,754
A method for the recovery of the carbon black from the stack gases when making furnace black.   C. O. C.

Carbon Black. Columbian Carbon Co.   *BP* 722,869
A process for producing furnace blacks of small particle size in large yield.   C. O. C.

Composite Lead Chromate–Lead Silicate Pigment. National Lead Co.   *USP* 2,668,122
A pigment having the excellent corrosion inhibiting properties of lead chromate but which is much cheaper to make is obtained by calcining a mixture of 2–10 mol. PbO per mol. CrO$_3$ and 0·75–7·5 mol. SiO$_2$ per mol. PbO.
C. O. C.

Titanium Dioxide. New Jersey Zinc Co.   *USP* 2,668,776
Increased drying rate and stability are imparted to TiO$_2$ by precipitating an aluminium orthophosphate *in situ* throughout an aqueous dispersion of the pigment.
C. O. C.

Rutile Titanium Dioxide. Titan Co.   *BP* 722,238
Before calcining metatitanic acid or raw TiO$_2$ to produce rutile pigment, a rutile promoter is added. This promoter consists of the coagulum of a colloidal Ti compound prepared by peptising Ti(OH)$_3$ with HCl or HNO$_3$ and coagulating the sol. so formed by adding metatitanic acid. This enables the peptising acid to be reused.
C. O. C.

Titanium Dioxide. DuP.   *USP* 2,670,272
USP 2,670,275
An improved method of producing pigmentary TiO$_2$ by burning TiCl$_4$ vapour in air.   C. O. C.

Differences and Analogies in the Chemical Constitution of Syntans and Leather Dyes (XII p. 203).

V—PAINTS; ENAMELS; INKS

Properties of well Defined Suspensions of Solids in Liquids. S. G. Ward. *J. Oil & Col. Chem. Assocn.*, 38, 9–42 (Jan. 1955).
A review of theoretical treatments of the viscosity and sedimentation of suspensions, in terms of various idealised systems; the measure of agreement with experimental findings is discussed also. Several graphs and tables of data are presented, and 49 equations are discussed. There is a full report of a lengthy discussion which followed the presentation of the paper, and an experimental demonstration with commentary by J. Pryce-Jones. A bibliography containing 51 references is given. J. W. D.

Emulsifiability of Offset Colours. J. H. Bitter. *Textil-Rund.*, 9, 650 (Dec. 1954).
To prevent the emulsification of offset colours in water, the colours should contain no polar material. The water used should be plain tap-water containing no wetting agent and with a pH of 5–6. A study of the effect of the

paper has shown that the only papers giving rise to emulsification are those which reduce the surface tension of tap-water by more than 15 dynes/cm. below its normal value.   J. C. F.

Fluorescent Coating Compositions. Photocolour
Laboratories.   *BP* 721,827
A hardenable resinous condensate and a fluorescent dye are dissolved in a volatile organic solvent in which has been dispersed a solid, colourless light-diffusing material insoluble in the solvent. There is < 35% by wt. of the resin in the total composition. The resin and dye must be in physical or chemical combination as determined by heating the dye (1 part by wt.) with the resin (99) in a volatile organic solvent for 30 min. at 75°c., forming a film from the solution and finally treating with a solvent for the dye which is a non-solvent for the resin when no dye should be dissolved out of the film.   C. O. C.

Fluorescent and Iridescent Wrinkle-finish Coating containing a Hydrous Iron Oxide Pigment.
New Wrinkle.   *USP* 2,668,799
Incorporation of a hydrous ferric-ferrous oxide or similar hydrous ferric oxide, e.g. the yellowish green pigments prepared as described in *USP* 2,335,760 into a suitable wrinkle base or with a base which after pigmenting will yield a wrinkle lacquer, yields a composition which dries to wrinkled films of good resistance to light and weathering and with an iridescent and multi-toned effect. Shading pigments, e.g. Cobalt Blue, may be used without impairing the iridescence, but addition of metal powders impairs the iridescence and may impart chalkiness.
                                                       C. O. C.

Pigmented Rolled Masses for Use in Lacquers.
Deutsche Gold- und Silber-Scheideanstalt vormals
Roessler.   *BP* 724,216
Pigments, especially Carbon Black, are readily incorporated in hydrocarbon-soluble high mol. wt. polymers, e.g. chlorinated polyvinylchloride or rubber hydrochloride, by friction rolling in presence of a guanidine derivative, especially a bis-guanide, as dispersing agent. The products are used for colouring lacquers.   C. O. C.

Oil-based Paint for Ceramic Surfaces. Dow Corning.
                                                   BP 722,484
A paint having satisfactory adhesion to ceramic surfaces contains an alkoxylated phenylmethyl organosilicon compound (25–35% by wt.), an unsaturated fatty acid of 12–20C and iodine number < 125 (20–30), glycerine (12–18), phthalic anhydride (25–40) and a solvent.   C. O. C.

Ceramic Colours for Application by Screen Printing.
B. F. Drakenfeld & Co.   *BP* 722,801
Modification of *BP* 648,209 (J.S.D.C., **67**, 168 (April 1951)). An enamel frit containing a ceramic colour is dispersed in a vehicle made up of a thermoplastic resin, a solvent and a wax. There is sufficient wax present to render the composition solid at normal temperatures but able to be melted for application while solidifying immediately after application.   C. O. C.

Liquid Burnish Gold for preparing Ceramic Transfers or for Direct Application to Heat-resisting Bases. R. S. Colour Works.   *BP* 721,906
A liquid burnish gold applicable either directly or by screen printing consists of finely divided gold powder suspended in a solution of a flux and, as adhesive, one or more oil-soluble sulphur-free resinates of Pb, Bi, B and Si. It has good covering power and the gold surface obtained after firing does not require buffing or etching to restore its brightness.   C. O. C.

Colour-stable Porcelain Enamel. Ferro Corpn.
                                                 USP 2,670,300
A porcelain enamel whose colour is the same whatever the temperature of firing consists of a titanium-opacified porcelain enamel containing 0·3–1·0% of Cr_2O_3 and 0·1–10·0% of a chromiferous pigment, e.g. an alkali chromate.
                                                       C. O. C.

Glass Colour Composition (IX p. 201).
Cellulose Trisalkylcarbamates (XI p. 203).
Epoxyalkoxyaryl Resins— Coating Compositions, Fibres, Foils, etc. (XIII p. 204)

VI— FIBRES; YARNS; FABRICS

Absorption of Water by Polymers. J. A. Enderby.
Trans. Faraday Soc., **51**, 106–116 (Jan. 1955).
A theory of water absorption by polymers possessing strongly hydrophilic groups is developed from consideration of statistical mechanics. The theory is applied to water absorption by cellulose. It is assumed that the initial tendency toward saturation in isotherms is due to hydrogen bonding between water and cellulose. The non-saturating part of the isotherm is assumed to be due to hydrogen bonding between water and either O atoms of cellulose or water molecules previously absorbed. A calculated isotherm is compared with low-humidity data for viscose rayon and cotton. The theory is compared with other theories of polymer absorption isotherms.   W. R. M.

New Aspects of Acetate Rayon. A. Sippel. *Melliand Textilber.*, **35**, 1317–1320 (Dec. 1954).
Some of the possible blends of acetate rayon staple fibre or filament are considered.   S. R. C.

Scientific and Technical Aspects of the Production of Bast Fibres. E. Emiliani and E. Vaccari. *Rev. Fac. Ing. quím.*, 21–22, 189–225 (1952–53): *Chem. Abs.*, **49**, 621 (10 Jan. 1955).
Review, 100 references.   C. O. C.

Pigmented Viscose Yarns, Films, etc. Kuhlmann.
                                                 BP 723,514
Modification of *BP* 711,977 (J.S.D.C., **70**, 423 (Sept. 1954)). Ultrafine dispersions of pigments in the cellulose ether used are obtained by dyeing the cellulose ether, e.g. with a vat or azoic dye, before dissolving it in the caustic soda.   C. O. C.

Acetate Crêpe Fabric. Eastman Kodak Co.
                                                 USP 2,669,766
Crêpe fabric having a permanent pebble, high textile strength and stretch and capable of being satisfactorily embossed or otherwise treated by the usual procedure in the production of crêpe fabrics, is obtained if the yarns it is made from consist of cellulose acetate filaments of initial high elongation and high tensile strength. Such filaments are obtained by extruding a volatile solvent solution of cellulose acetate and curing the resulting filaments under minimum tension.   C. O. C.

Linear Polyamides having Good Affinity for Dyes containing Acid Groups. Bobingen A-G. für Textil-Faser.   *BP* 723,130
Linear polymers containing within the chain a number of –NH·CO– groups separated from each other by several methylene groups and having (a) within the chain several subst. or unsubst. benzimidazole or benzodi-imidazole nuclei, their number being > ¼ that of the –NH·CO– groups or (b) as chain terminating groups, similar groups, in number > $\frac{1}{15}$ that of the –NH·CO– groups have very good affinity for acid dyes. They are much more suitable than nylon for dyeing with afterchrome dyes.   C. O. C.

Highly-elastic N-alkyl substituted Polyamide Fibres.
DuP.   *USP* 2,670,267
Highly elastic fibres are obtained if oriented filaments of N-alkyl substituted polyamide (Alk of > 1 C) are heated to 60–80°c. in water or air at high R.H. and then similarly heated to 90–100°c. This enables shrinkage under boil-off conditions to be reduced to 2–5%.   C. O. C.

Resilient Polyethylene Terephthalate Fibres. DuP.
                                                 BP 721,912
Polyethylene terephthalate fibres are given wool-like characteristics by drawing them to 90–100% of the highest possible draw ratio obtainable at 35–50°c. while they are wet with a hydroxylated non-solvent, preferably water.   C. O. C.

Terpolymers of Acrylonitrile, 1-Vinylimidazole and a Monomer containing the >C:C< Linkage.
Chemstrand Corpn.   *BP* 723,538
The terpolymers of < 50% of acrylonitrile, > 2% of 1-vinylimidazole and 1–18% of a monomer containing the > C:C < linkage, e.g. vinyl acetate, are readily dyed with acid dyes. They are used for making fibres, either alone or incorporated into polyacrylonitrile, in coating compositions, etc.   C. O. C.

Cellulose Trisalkylcarbamates (XI p. 203).

Stabilising Nylon to Heat and Oxygen (XIII p. 204).

Epoxyalkoxyaryl Resins—Coating Compositions, Fibres, Foils, etc. (XIII p. 204).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Permeability of Regenerated Cellulose Membranes to Sodium Dodecyl Sulphate Solutions. B. S. Harrap and J. J. O'Donnell. *J. Physical Chem.*, 58, 1097–1099 (Dec. 1954).

Purified sodium dodecyl sulphate, on dialysis in the presence of salt, does not distribute itself equally across a Cellophane membrane when the total concentration is above the critical micelle concentration. It is suggested that the solution inside the dialysis bag contains micelles plus single ions, whereas that on the other side of the membrane contains single ions only. The size of the micelles decreases with decreasing salt concentration to such an extent that, in the absence of salt, diffusion of micelles through the membrane occurs, resulting in equal concentrations of detergent on both sides of the membrane at equilibrium. Certain commercial detergents cannot be completely removed from solution by dialysis.

W. R. M.

Viscometric and Turbidimetric Measurements of Dilute Aqueous Solutions of a Non-ionic Detergent. L. M. Kushner and W. D. Hubbard. *J. Physical Chem.*, 58, 1163–1167 (Dec. 1954).

Viscosities and turbidities of dilute solutions of a non-ionic detergent (a polyoxyethylene condensate of an octylphenol) have been determined in water and in 0·04 and 0·12 M-NaCl. The molecular weight of the micelles is 90,000 and independent of added salts. Results are interpreted in terms of a highly hydrated spherical micelle of radius equal to the length of a nearly extended detergent molecule. W. R. M.

Micellar Molecular Weights of Surface-active Agents. A. M. Mankowich. *J. Physical Chem.*, 58, 1027–1030 (Nov. 1954).

Using light scattering methods, micellar molecular weights of six anionic and non-ionic surface-active agents have been determined in aqueous solution in the concentration range 0·2–1·0%. The possibility of a continuous change in micellar size with increasing concentration is suggested. The effects of one alkaline and two neutral builders on the micellar size of an alkyl arylsulphonate are found to be considerable. W. R. M.

PATENTS

Bleaching Chemical Wood Pulp. DuP. *BP* 2,668,095

In the multi-stage bleaching of chemical wood pulps a better and more permanent bleach is obtained if the pulp is acidified between an earlier stage where it is treated with a calcium compound and a later stage where it is treated with alkaline peroxide. C. O. C.

Bleaching Coir. N. V. Amsterdamsche M-S tot Exploitatie van Octrooien. *BP* 722,597

Bleaching coir with aqueous hydrosulphite at 70–90°c. immediately after the fibre has been separated from the pitch or coir dust removes the tannic acid content and so reduces discoloration of the fibres during subsequent processing. C. O. C.

Bleaching Powdered Hoof, Horn or other Keratinous Material. Rochester Button Co. *USP* 2,667,475

Improved bleaching with less use of hydrogen peroxide is obtained if the hydrogen peroxide-decomposing enzyme or catalase in the material is first destroyed or inactivated. A good method of doing this is to heat an aqueous suspension of the finely ground hoof or horn to < 120°F.

C. O. C.

Dry Cleaning. Metallgesellschaft. *BP* 721,917
BP 722,379

Addition to benzene, or chlorinated hydrocarbons, of organic derivatives of phosphoric acid which are soluble in it, e.g. cetylorthophosphate, increases its cleansing power, enables small amounts of water to be added to the liquor and greatly reduces the tendency for electrostatic charges to be formed. C. O. C.

Mechanical Aid for Wet Processing in the Finishing Industry (I p. 190).

VIII— DYEING

High-temperature Dyeing. J. P. Niederhauser. *Teintex*, 12, 891–911 (Dec. 1954).

Pressure machines use auxiliary pumps, compressed air, or steam. The problem of shading is met by dyeing a small sample of substrate in a vessel which may be isolated from the circuit, or by including a valve through which filament may be drawn without appreciable loss of pressure in the main vessel. Experiments with acid, chrome, direct, sulphur, vat, azoic, disperse, and basic dyes are described. 74 references. S. R. C.

Neutralisation of Diazo Solutions with Chalk. E. Fedorova and E. I. Sheludyakova. *Tekstil. prom.*, 14, 26–29 (Feb. 1954): *Textil Praxis*, 9, 968–971 (Oct. 1954).

Sodium acetate can be replaced by chalk in the neutralisation of diazo solutions containing HCl, the diazo compound being stabilised by the calcium chloride so formed. This process can be used in printing without damaging the fibre. Zinc oxide and magnesium oxide can be used instead of chalk, when the diazo solution is stabilised by the corresponding metal chloride. Neutralisation of the diazo solution containing sulphuric acid does not give a stabilised diazo compound, and decomposition of the diazo compound could give rise to mineral acidity, which damages the fibre. C. H. R.

Continuous Dyeing with special reference to Micro-disperse Vat Dyes [The Pad–Roll Process]. M. Peter. *Tex*, 13, 1510–1519 (Dec. 1954).

A description of continuous dyeing processes including pigment padding, the Williams unit, and the hot oil process. Special attention is paid to the use of micro-disperse Cibanone (Ciba) dyes, which are anthraquinone vat dyes in a very fine state of homogeneity and dispersion, the particle size being 0·2–1μ., and which are applicable in the above processes. Details are given of the Swedish "pad–roll" process, in which the material is padded cold in a short liquor, dried on both sides at 100–102°c. with infrared driers, rolled up, and treated in a chamber at 100–102°c. with saturated steam to fix the dye. The cloth passes through the pad at 40–60 metres/min. at 100–110% take-up. The machine is not fully continuous, and 4000–5000 metres of cloth is made into the roll before fixation. The machine is suitable for applying direct dyes to cellulosic materials, disperse dyes to acetate rayon, and neutral-dyeing premetallised (Cibalan) dyes to wool. B. K.

Effect on Wool of Boiling in Aqueous Solutions. II— Solutions of Ammonium Salts with and without Ammonia. R. V. Peryman. J.S.D.C., 71, 165–170 (April 1955).

The pH values at 100°c. obtained by extrapolation from measurements on dilute aqueous solutions of ammonium sulphate, acetate, (diammonium) phosphate, chromate, and chloride at temperatures ranging from 18° to 80°c. agree approximately with the pH values at 100°c. calculated from the published dissociation constants of the acids, ammonium hydroxide, and water. It follows that pH measurements on the solutions at room temperatures cannot, without other data, be relied upon to indicate their pH values at 100°c. Ammonium salt solutions containing added ammonia can have pH values ca. 2 units lower at 100°c. than at 18°c. Ammonium sulphate–ammonia solutions of alkaline pH values ≯ 8 when measured at 18°c. have acid pH values < 6 at 100°c. without loss of ammonia. Metachrome mordant solutions with room-temperature pH values ca. 6·7–8·7 are at 100°c. buffered at ca. pH 6·7.

Wool yarn, boiled for 3 hr. in the ammonium salt and ammonia solutions (excluding chromate and chloride) at controlled pH values and at concentrations simulating commercial dyeing, gives degrees of modification, as measured by wet breaking load and content of disulphide sulphur, in fair agreement with the salt contents of the solutions and the pH values at 100°c. but not with the pH values at room temperature. AUTHOR

Influence of Fluorescent Lighting on Fluorescently Brightened Textiles. F. Gasser and F. Weber. *Melliand Textilber.*, 35, 1362–1364 (Dec. 1954).

Prolonged illumination by fluorescent tubes, designed to simulate shop-window and stores conditions, produced no fading or loss of tensile strength of textiles treated with fluorescent brightening agents. S. R. C.

Dyeing and Impregnating Textile Webs. K. Scheller.
BP 720,701

Two rollers, independent of each other, are in operative connection with a third roller so as to form two nips. This enables the pressure exerted at each nip to be varied independently of the other. Two of the rollers form a chamber for dyeing or processing liquid that is independent of the liquid trough. This enables small batches of goods to be treated economically.   C. O. C.

Simultaneously Dyeing and Presetting Tricot Fabrics. American Viscose Corpn.   USP 2,669,502

The edges of the fabric are uncurled and it is then passed in open width through a dyebath which also acts as a setting bath. In the bath it is so held that curling of the fabric edges is prevented until the strains in the fabric have been relaxed.   C. O. C.

Improving the Wet Fastness of Direct Dyeings. FBy.
BP 721,238

The wet fastness of direct dyeings is much improved by treatment with the condensation product of a salt of guanidine or dicyandiamidine, an aliphatic aldehyde and cyandiamide, dicyandiamide, melamine, urea or thiourea, condensation being carried out in weakly acid or neutral medium in presence of an ammonium or monoamine salt.
C. O. C.

Dyeing Loose Wool. Ciba.   BP 722,821

Tippy dyeing is avoided when dyeing with metalliferous dyes or with metallisable dyes if the wool is treated before or during dyeing with the reaction product of < 4 mol. of an $\alpha\beta$-alkylene oxide with 1 mol. of an organic compound containing at least one basic primary or secondary amino group or containing a basic tertiary amino group and an alcoholic hydroxy group.   C. O. C.

Dyeing Polyethylene Terephthalate Fibres with Disperse or Vat Dyes. General.   USP 2,670,263

When dyeing Terylene with vat or disperse dyes complete penetration of the fibre combined with deeper and brighter dyeings is obtained if xylene, naphthalene, chlorobenzene, o-dichlorobenzene or trichlorobenzene is used as a carrier in presence of an emulsifying agent in an aqueous bath at 195–212°F.   C. O. C.

Hair Dyeing or Tinting. Ashe Laboratories.
BP 721,831

Level dyeing acid dyes are applied at room temperature in aqueous solution at pH 7–11 in presence of a mercaptan which relaxes or softens the hair. This gives strong dyeing of the hair (greater than is obtained with a hot acid liquor), the dyeing being fast to shampooing. This enables dyeing to be combined with cold permanent waving, the effect of oxidising agents being to improve the fastness of the dyeing.   C. O. C.

Staining Glass. Verd-a-Ray Processing Co. BP 720,979

The glass is coated with a liquid dispersion containing copper, silver and zinc salts and then heated to 800–1100°F. The proportion of salts in the dispersion is, calculated as the metals, on the total metal present, Cu 15–90%, Ag < 0·875% and Zn < 1·7%. The dispersion should also contain 1·4–115·0% Cl based on the weight of metals present.   C. O. C.

Dissolving or Dispersing Substances in Liquids or Semi-liquids—Colouring Butter or Margarine. Dyestuffs & Chemicals.   BP 723,450

The substance, e.g. FD&C Yellow No. 3 or 4, is mixed with starch and compressed into a tablet of density < 1. Such tablets, when added to the churn rapidly and completely, colour the butter without any dark specks remaining.   C. O. C.

Mechanical Aid for Wet Processing in the Finishing Industry (I p. 190).
Flameproofing Composition for Cellulosic Materials (III p. 191).
Pigmented Viscose Yarns, Films, etc. (VI p. 198).

IX— PRINTING

Roller Printing of Cellulose Acetate Fabric. W. B. Miller. Dyer, 112, 1015–1021 (10 Dec. 1954).

The hydrophobic character of cellulose acetate presents difficulties in roller printing not encountered with cotton or viscose rayon. Finer scale and shallower depth of engraving are necessary than is the case when printing cotton; also, wider engraving allowances must be made in order to prevent overlap flushing. The increase in area of acetate rayon when wet makes it essential that the rollers should be correctly positioned in the machine if perfect registration is to be obtained. Coloration with disperse, acid, and vat dyes is discussed, and suitable types of steaming and washing-off apparatus are described.
A. H.

Development of Indigosols. V. E. Rostovtsev. Tekstil. prom., 14, 34–36 (April 1954): Textil Praxis, 9, 1169–1171 (Dec. 1954).

Chloramine B and T have been found to be satisfactory under bulk conditions for the development of direct prints of Indigosols. Pretreatment of cotton with chloramine can also be used for subsequent dyeing with Indigosols, and recipes are included for white and colour resists using this procedure. No damage to cotton has been detected by pretreatment with chloramine solution (50 g./litre) and subsequent drying at 70–80°C.   B. K.

Investigations on Colour Development. XII— Influence of Traces of Copper on the Oxygen Oxidation of Colour Developers and Hydroquinone Solutions containing Sulphite. K. Meyer and L. Roth. Z. wiss. Phot., 49, 10–16 (1954): Chem. Abs., 49, 81 (10 Jan. 1955).

Previous work on the O_2 oxidation of p-aminodiethylaniline sulphate (I) in presence of Na_2SO_3 showed that sulphite : I oxidised :: 2 : 1. The Na_2SO_3 used contained 56 μg. Cu per 100 g.; thus Cu catalysed the O_2 oxidation of sulphite. Direct oxidation of sulphite in K_2CO_3 soln. is greatly decreased by presence of Trilon B, which prevents the Cu catalysis. At lower pH, Trilon B retards oxidation of sulphite, but its effectiveness decreases with pH over the range 8·3–6·5. Trilon B does not retard oxidation of I in absence of sulphite. Air oxidation of a solution of 2·6 g. I, 2·5 g. Na_2SO_3, and 2 g. Trilon B was followed analytically. Sulphite : I oxidised :: 1 : 1. The molecular ratio sulphite : Trilon B was then varied. For ratios 2 : 1, 2 : 0·01, 2 : 0·001, 2 : 0·0001, the ratios of I : sulphite oxidised were 1 : 1·01, 1 : 1·06, 1 : 1·46, 1 : 2·10. Rate of oxidation of I was the same in all developers. Experiments with hydroquinone–Na_2SO_3 developers showed that the ratio of sulphite : hydroquinone oxidiser varied from 1·7 to 2·0 in absence of Trilon B and from 1·1 to 1·2 in its presence. Apparently no direct oxidation of sulphite to sulphate occurs when Cu catalysis is prevented, and the O_2 oxidation of I can be formulated—

$(C_2H_5)_2N \cdot C_6H_4 \cdot NH_2 + Na_2SO_3 + O$
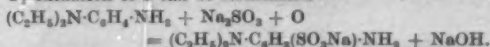
$$= (C_2H_5)_2N \cdot C_6H_3(SO_3Na) \cdot NH_2 + NaOH.$$
C. O. C.

Screen Printing in America. Anon. Dyer, 112, 589–594 (15 Oct. 1954).

A description of the processing of cloth in an American works includes a full description, illustrated by photographs, of the Fritz Buser automatic screen-printing machine.   A. H.

Validity of Beer's Law for Agfacolor Film. L. Friedrich. Z. wiss. Phot., 49, 114–118 (1954): Chem. Abs., 49, 83 (10 Jan. 1955).

Samples of each of the three emulsions of negative Agfacolor B and of positive Agfacolor were separately exposed under a sensitometer wedge and developed to the respective yellow, magenta, or cyan image. Density photos were made for each sensitometer step from 400 to 700 mμ., corrections being made for the densities of the gelatin and support. The densities of the dye images follow closely those predicted by Beer's law. The agreement is not as good with the yellow and magenta images as with the cyan, but the divergencies are too small to have significance in practical colour photography.
C. O. C.

Pigmented Emulsion for Fabric Printing. Sun Chemical Corpn.   USP 2,668,159

The continuous phase consists of a lacquer or a solution of a thermosetting resin in an organic solvent in which is dispersed a plastisol of a synthetic thermoplastic resin which is insoluble in the solvents of the continuous phase. The plastisol is made by dispersing the thermoplastic resin in non-volatile liquid plasticisers. The disperse phase

consists of pigment and water. The finished prints have good fastness to rubbing, dry cleaning and washing.

C. O. C.

Light-sensitive Material for preparing Printing Screens. Kodak. *BP 721,071*

A flexible transparent support is coated first with a gelatino-silver halide emulsion and then with a second such emulsion containing a non-migrating yellow colouring material dispersed in it. After this assembly has been exposed to light and a relief image formed in it, it is pressed onto the printing screen, dried and the support removed leaving the image on the screen. This method makes adequate exposure possible without hardening the gelatine too much. C. O. C.

Colouring Embossed Fabric. Rock Mill Printing & Finishing Co. *USP 2,667,426*

The fabric is passed through an embossing calender and while still on one of the calender rolls is treated with another roll travelling at the same surface speed as the calender rolls which applies colour to it. If it is desired that the colour shall be applied to the raised portions of the embossed design then the colour-applying roll has a smooth surface but if the colour has to be applied to the sunk portions of the design, then the colour-applying roll has an appropriately relieved surface. C. O. C.

Improving the Adhesion of Printing Inks to Plastic Film. Visking Corpn. *BP 722,875*

Both surfaces of the film are evenly treated by passing it through a zone of action of high voltage electric stress accompanied by corona discharge. The treated film is apparently unaltered in any characteristic, but when it is printed the prints are unaffected either by the "Scotch" tape test or by contact with fats for two days. The process is particularly applicable to polyethylene film. C. O. C.

Restoring Used Colour-reactant Record Material for Reuse. National Cash Register Co. *USP 2,669,503*
BP 720,616

Used colour-reactant record material sensitised with an acid-like electron-acceptor adsorbent pigment, e.g. NaAl silicate and discoloured by application of a mixture of a double-bond aromatic organic compound which is an electron-donor with respect to the pigment, e.g. 3:3-bis-(p-dimethylaminophenyl)-6-dimethylamino phthalide, and an inorganic compound which in contact with the pigment slowly oxidises to form a colour faster to light and air than that formed by the pigment and the first organic compound, e.g. tetramethylbenzene, can be decolourised and made available for reuse by treating it with a volatile acid to convert the coloured marks to a colourless salt with consequent desorption of the salt from the pigment and finally washing with a volatile solvent to remove the unoxidised oxidisable colour-reactant present. C. O. C.

Glass Colour Composition. DuP. *BP 721,858*

A glass colour which hardens rapidly comprises as vehicle stearic acid (30–60%), stearyl acid phosphate (2–7), ethyl cellulose (0·1–10·0), hydrogenated rosin (15–40) and polymerised rosin acids, e.g. pimaric and abietic acid, (10–30) and as colour inorganic oxide pigment (5–20) and finely-ground glass frit (95–80) the proportion of colour to vehicle being 1–6 : 1. It is suitable for application by screen printing and dries so quickly that successive superimposed layers can be applied with great rapidity.

C. O. C.

Printing Resilient Articles. Dunlop Rubber Co. *BP 723,030*

A solvent for the printing medium is applied to part of the surface of e.g. a rubber ball, a printing composition is then applied to the same part of the surface and the ball is dried. Apparatus is described in which the goods are fed *seriatim* to the solvent applying means, to the printing mechanism and to the drying chamber. C. O. C.

Furoquinoxalines and Thienoquinoxalines as Catalysts in Dye Bleach Baths for Colour Photography. General Aniline. *USP 2,669,517*

Compounds of formula—

(A = O or S; Z^1 and Z^2 = atoms to complete a carbocyclic aromatic ring system) are highly effective catalysts for silver dye bleach baths, non-substantive to gelatin, non-staining and without effect on the quality of the final image.

C. O. C.

2-Substituted Indazolones as Colour Couplers (IV p. 195). Requirements of Printing Paper in the Light of Recent Research (XI p. 202).

X— SIZING AND FINISHING

Preparation and Properties of Regenerated Cellulose containing Vinyl Polymers. II— Staining, Swelling, and Stiffness Characteristics. G. Lardells and C. S. Whewell. J.S.D.C., 71, 171–174, (April 1955).

Staining and swelling tests have confirmed that vinyl polymers may be readily deposited inside viscose rayon filaments and that different degrees of penetration are obtained depending on the properties of the monomer employed. Vinyl polymers increase the stiffness of viscose rayon filaments, and as increasing amounts of polymers are deposited internally the filaments become increasingly distended. About 8% of polymer may, however, be introduced without causing any change in the diameter of the fibres. AUTHORS

PATENTS

Improving the Dimensional Stability and Wet Strength of Regenerated Cellulose Textiles. Algemene Kunstzijde Unie. *BP 721,380*

The material is impregnated with an aqueous solution containing, by weight, 4–10% of a dialdehyde in which the aldehyde groups are separated by a chain of 3–7 C atoms, e.g. α-hydroxyadipaldehyde, and 0·3–1·2% of a weakly ionisable, organic acid catalyst, dried at < 100°c. and baked at > 100°c. This confers dimensional stability without impairing the other physical properties of the material. C. O. C.

Rendering Cellulosic Materials Flame-resistant. National Lead Co. *USP 2,668,780*

The material is impregnated with an aqueous solution of incompletely substituted chlorides of tetravalent Ti, dried sufficiently to cause the solution to form a transparent gel on the material, then treated with an alkaline agent and finally washed and dried. An improved effect both in resistance to flame and to afterglow is obtained if $SbCl_3$ is also present in the solution. The finish is fast to repeated washing. C. O. C.

Flame-resistant Fibrous Aminoethylated Cellulose. U.S. Secretary of Agriculture. *USP 2,668,096*

Aminised cellulose fibres containing primary amino groups are treated simultaneously with tetrakis(hydroxymethyl)phosphonium chloride and melamine, guanidine or urea and with formaldehyde.

The phosphonium chloride reacts simultaneously with the cellulose to yield a cellulose derivative containing both P and N, and with the polyamino compound and with the formaldehyde. The products have the same handle as aminised cellulose but are more flame-resistant, this property being little affected by laundering. C. O. C.

Reducing the Tendency of Wool to Felt. DuP. *USP 2,678,286*

The wool is impregnated with a high mol. wt. substituted hydrocarbon polymer or like addition agent and with a fixative after which it is cured, e.g. impregnated with 2–10% by wt. of a chlorinated polymer of ethylene and 0·01–0·1% of an organic compound containing polyhydroxy, polymercapto, polyamino or polyamide groups and baked at 75–250°c. C. O. C.

Deacetylated Chitin for Reducing the Felting Property of Wool. Montclair Research Corpn. and Ellis-Foster Co. *USP 2,669,529*

The wool is impregnated with 1·5–10·0% of its weight of undegraded partly deacetylated chitin and baked at 110–140°c., the chitin being applied as a salt from aqueous solution. C. O. C.

Setting Wool Fabrics. Pacific Mills. *USP 2,669,002*

Wool fabric is continuously set by impregnating it with 50–60% of its own weight of an aqueous solution at pH 9–12, e.g. a sodium hydroxide solution buffered with disodium phosphate, in a three-roll mangle, passed under

a dancer roll where the warp ways tension is adjusted and tentered. During tentering the fabric is heated, e.g. by passing between banks of infrared lamps, so that steam is generated in its interior, this steam co-acting with the liquid in the fabric to cause setting. C. O. C.

Coating with Aqueous Protein Compositions. Kodak. *BP* 721,064

An aqueous solution of protein is used containing (on the wt. of protein) 0·5–5·0% of formaldehyde, acrolein or glyoxal. After application it is set by treatment with gaseous ammonia. This yields a clear coating which is set before drying and without chilling being necessary. C. O. C.

Surface Treatment of Leathercloth made of a Vinyl Resin. Dunlop Rubber Co. *BP* 721,303

Embossed vinyl resin leathercloth is coated with the gel formed by a polymer or copolymer of vinyl chloride and a volatile ester of a fatty acid of < 6 C after which the ester is removed. When a pigmented gel is used, the process is particularly suitable for the production of an antique effect. C. O. C.

Coating Threads with Metals. National Research Corpn. *BP* 721,879

The threads are placed in a vacuum chamber, preferably being arranged warp-wise. The chamber is evacuated and metal vaporised in it, e.g. Al is heated to about 1300°c. The threads are then passed through the vapour stream, each thread being rotated as it passes through the vapour to ensure complete coating. They are then coated with a transparent protective composition which does not decrease the infrared radiation reflecting powers of the metal film. C. O. C.

Mechanical Aid for Wet Processing in the Finishing Industry (I p. 190).
Electrical Wet Heat Treatment of Materials having Poor Electrical Conductivity (I p. 190).
Acetate Crêpe Fabric (VI p. 198).
Dyeing and Impregnating Textile Webs (VIII p. 200).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Requirements of Printing Paper in the Light of Recent Research. G. Carlsson. *Textil-Rund.*, 9, 628–639 (Dec. 1954).

After briefly discussing the properties which govern the behaviour of a paper in printing, the author reviews recent work done at the Graphical Research Laboratory, Stockholm. A consideration of the partition of the ink film between the surface of the forme and the paper leads to the introduction of the ink transfer index (y) defined as the ratio (quantity of ink transferred to paper)/(quantity of ink remaining on forme). The dependence of y on the quantity of ink initially on the forme shows qualitative differences for different types of paper. The index y increases with increasing pressure on the forme, tending to a constant value at high pressures. Generally, y decreases with increasing ink viscosity and with increasing printing speed. The absorptive qualities of paper for printing ink and for high-viscosity mineral oils are found to be similar. As the properties of such oils are more reproducible than those of inks, the effect of sizing treatment on oil absorption has been studied. The rate of oil absorption is increased by sizing with starch or resin, but the rate is decreased by sizing with carboxymethylcellulose. Surface strength and opacity requirements of printing paper are also discussed. J. C. F.

Degradation of Cellulose by Ionising Radiation. A. Charlesby. *J. Polymer Sci.*, 15, 263–270 (Jan. 1955).

When subjected to ionising radiation, cellulose is rapidly degraded to a powdery material. A theoretical treatment shows that, if the effect of radiation is to cause random fracture in the main chain, the relation between intrinsic viscosity $[\eta]$ and radiation dose R should be—

$$\log [\eta] = -a \log (R + R_0) + \text{const.}$$

where R_0 is a "virtual" radiation dose required to produce the initial number-average molecular weight from a chain of infinite mol. wt. Published data are used to verify this

formula, which leads to a relationship between $[\eta]$ in cupriethylenediamine and viscosity-average mol. wt.—

$$[\eta] = KM_v{}^a$$

with $a = 0.71$. W. R. M.

Chemistry of Cuprammonium Solutions of Cellulose. VI— Question of Presence of Copper–Cellulose Anion (containing Cu–O–C) in Cuprammonium Cellulose Complexes. S. N. Danilov and M. G. Okun'. *J. Gen. Chem. U.S.S.R.*, 24, 2153–2164 (Dec. 1954).

Electrolysis experiments, with and without a porous membrane between anode and cathode spaces, on cuprammonium soln. of cellulose (with and without addition of NaOH), methyl cellulose, hydroxyethyl cellulose, alginic acid, tartaric acid, glucose, sorbitol, and glycerol indicate that no copper-containing anion is formed, separation of copper occurring only at the cathode. It is considered that the experiments support the view that cuprammonium cellulose complexes are quite analogous in structure to those formed with caustic alkalis, and cuprammonium soln. of polysaccharides are similarly analogous to aq. caustic alkali soln. [cf. method and conclusions of Neale, *J. Textile Inst.*, 16, T 363 (1925)]. The hypothesis is further confirmed by adsorption experiments with anion- and cation-exchange materials. Absorption of ammonia and copper, and precipitation of cellulose, occur only on the cationites; the soln. pass unchanged through anionites. A. E. S.

Reaction of Cellulose with Acetic Acid. L. A. Hiller. *J. Polymer Sci.*, 14, 555–577 (Dec. 1954).

Reaction curves for the reaction of cellulose with acetic acid and water have been studied. The reaction is found to be slow and severely limited in extent. An analysis by means of reaction kinetics equations for this limited reaction leads to the following suggested mechanism— (a) the larger proportion of cellulose hydroxyl groups cannot be acetylated because hydrogen bonding between these groups imposes an energy barrier to the reaction; (b) part of the remaining hydroxyl groups which do react do so very slowly with a reaction rate apparently dependent on the rate of diffusion of acetic acid into the cellulose fibres, these hydroxyl groups being apparently unassociated ones buried within the cellulose fibres; (c) the remaining hydroxyl groups apparently react according to the kinetics of homogeneous acetylation and must be in freely accessible positions. W. R. M.

Sorption of Nitrogen Dioxide by Cellulose Acetate. W. J. Myles and H. Reiss. *J. Polymer Sci.*, 15, 243–261 (Jan. 1955).

Sorption of NO_2 by cellulose acetate proceeds by a process of solution, diffusion, and reaction governed by Henry's law, Fick's law, and first-order kinetics with respect to consumption of NO_2. Water appears to be the primary substrate with which NO_2 reacts in cellulose acetate. The solubility of NO_2 in dry film decreases with increasing degree of acetylation. The diffusion coefficient and the solubility in moist films are determined as a parameter jointly involving them. W. R. M.

Interaction of Organophosphorus Compounds with Solvents and Cellulose Acetate. A. L. Geddes. *J. Physical Chem.*, 58, 1062–1066 (Dec. 1954).

The infrared spectra of several organophosphorus compounds in various solvents and in cellulose acetate are reported and band frequency assignments in the region 2–15 μ are discussed. Information on molecular interaction is obtained from band frequency shifts. Results are interpreted as evidence for (1) hydrogen bonding between hydroxyl and phosphoryl groups and (2) dipolar interaction between phenyl and carbonyl groups. W. R. M.

Solvent Power of Solvents for Cellulose Nitrate. W. R. Moore and J. A. Epstein. *J. Appl. Chem.*, 5, 34–39 (Jan. 1955).

A comparison, for soln. of cellulose nitrate (12·2% N) in alkyl methyl ketones and alkyl acetates, of various methods of estimating "solvent power", viz. those based on osmotic pressure data (Huggins interaction const.), on inert-diluent toleration, and on viscosity–concn. relations. A. E. S.

Effect of Metal Ions on the Properties of Ethyl-cellulose. III—Dependence of the Viscoelastic Characteristics of Ethylcellulose Gels on the Content of Sodium Ions. S. A. Glikman, O. G. Efremova, and V. M. Aver'yanova. *J. Gen. Chem. U.S.S.R.,* 24, 1427–1432 (Aug. 1954).

Addition of 0·1% of Na⁺ ions to pure ethylcellulose results in effects (increase in the elastic moduli and viscosity of its gels in dibutyl phthalate) similar to those found previously (see J.S.D.C., 68, 329 (1952)) for the addition of much lower amounts of Ca²⁺ and Fe³⁺. Addition of Na⁺, like that of Ca²⁺, has no effect on the viscosity of a soln. in a mixed solvent having a polar component (it was previously found that the presence of traces of Ca²⁺ leads to increase in the viscosity of soln. in non-polar solvents).   A. E. S.

Molecular State of Benzylcellulose Solutions. H. B. Roy. *J. Indian Chem. Soc.,* 31, 485–494 (July 1954).

Osmotic pressure measurements on soln. of benzyl-cellulose in chloroform at 40° and 50°c. show that there is no change in mol. wt. of the ether with increase in temp., but the slope of the osmotic pressure–concn. curves changes from negative to positive. This is explained by assuming that the ether molecules are coiled, with intramolecular cross-linkages which are broken, with consequent unfolding of the molecules, as the temp. increases. With ethyl acetate as solvent, the mol. wt. decreases over the temp. range in addition to a change of slope. It is assumed that in this solvent cross-linkages are intermolecular. The addition of small amounts of ethanol to the chloroform soln. causes no change in apparent mol. wt. but changes the slopes of the osmotic pressure curves to a more positive value. With ethyl acetate soln. the mol. wt. is lowered on addition of ethanol. The intrinsic viscosity of chloroform soln. increases with increasing temp., again suggesting the unfolding of curled-up, non-aggregated molecules, whereas with ethyl acetate as solvent the intrinsic viscosity decreases with increasing temp., suggesting a breakdown of molecular aggregates. The effect of additions of ethanol tends to support these conclusions.   A. J.

PATENT

Cellulose Trisalkylcarbamates. DuP. *USP* 2,668,168

Natural or regenerated cellulose is completely esterified by treating it at 80–160°c. with a large excess of alkyl isocyanate dissolved in methyl formamide. The products are soluble in many organic solvents, particularly methyl-formamide, and may be extruded to form fibres or films. The films are transparent and hydrophobic. On being treated with aqueous formaldehyde they become insoluble in organic solvents. They can be used for sizing and finishing textiles, coating paper, lacquers, etc.   C. O. C.

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Differences and Analogies in the Chemical Constitution of Syntans and Leather Dyes. H. Loewe. *Rev. Tech. Ind. Cuir,* 46, 251–256 (Dec. 1954).

The tanning action of syntans depends upon the formation of hydrogen bonds with the carbonyl groups of collagen, the possession of a dipole of opposite sense to that of the peptide group, and mol. dimensions sufficient to allow "bridging" between collagen chains. These attributes are possessed also by many simple aniline dyes; the tanning action of certain dyes is well known. The structural similarities and differences between a number of syntans and simple dyes (including Orange GG, Croceine Scarlet, Diamine Fast Brown GB, Sirius Light Yellow RT, and Fuchsin) are discussed in terms of the tanning ability of these cpd.   J. W. D.

Theoretical Rules governing the Co-ordination of Ligands to Chromium. S. G. Shuttleworth. *J. Soc. Leather Trades Chem.,* 38, 419–425 (Dec. 1954).

There has in the past been much confusion and inter-change of terms such as "co-ordination", "hydrogen

bonding", and "adsorption" in the field of chrome tanning theory. Existing evidence is collated, and five rules are derived which serve as a general guide to Cr complex formation and the mechanism of chrome tanning. Some of the work cited exists only as unpublished theses. The five rules are— (i) In order to compete successfully with co-ordinated water mol. on the Cr ion in aq. soln. (where water predominates) O atoms must acquire additional electronegativity through a negative charge. (ii) The stability of co-ordination of an acidic group to Cr is inversely proportional to the dissociation constant of the acid. (iii) Amine groups do not co-ordinate appreciably to Cr under aq. acid conditions, and even under neutral aq. conditions their Cr co-ordination stability is much less than that of COOH. (iv) The formation of chelate rings greatly enhances the co-ordination stability. (v) The stability constants of co-ordinated ligands follow a step-wise pattern of decreasing affinity in respect of the six co-ordination bonds of tervalent Cr. These rules have wide implication in the theory of chrome tannage and the masking action of various ligands. Only the COOH groups of collagen are likely to co-ordinate to Cr ions under the aq. acid conditions of normal tannage, but if steric factors are suitable the carbonyl and side-chain oxygens and the uncharged nitrogens may participate to some extent during drying.   J. W. D.

Action and Method of carrying out Acid Pickling in the Dressing of Fur Skins. F. Stather, H. Herfeld, and S. Beyer. *Ges. Abh. dtsch. Lederinst.,* (10), 52 (1954): *J. Soc. Leather Trades Chem.,* 38, 429 (Dec. 1954).

Tests were performed with different acid concentrations with and without formaldehyde pretreatment, on the pickling of fur skins.   C. J. W. H.

PATENTS

Water-soluble Phenol–Formaldehyde–Borax Condensates—Tanning Agents. American Cyanamid Co.   *USP* 2,667,466

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C. O. C.

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XIII—RUBBER; RESINS; PLASTICS

Temperature Dependence of Compression of Linear High Polymers at High Pressures. C. E. Weir. *Bur. Stand. J. Res.,* 53, 245–252 (Oct. 1954).

Pressure–volume–temperature data for a number of ethenoid polymers and a polyester are reported over the range 20–80°c. and 1–10,000 atm. Empirical equations of state are derived for some of the polymers.   W. R. M.

Macromolecular Compounds. LXVII—Properties of Polyesters derived from Dicarboxylic Acids and Polymethylene Glycols. LXVIII—Effect of the Introduction of Ether Oxygens and Side-chains into Polyesters. V. V. Korshak, S. V. Vinogradova, and E. S. Vlasova. *Izvestiya Akad. Nauk S.S.S.R., Otdel. khim. nauk,* 1089–1096, 1097–1102 (Nov.–Dec. 1954).

LXVII— Polyesters are prepared by reaction under constant conditions of OH·[CH₂]ₘ·OH (m = 2, 6, and 10) with COOH·[CH₂]ₙ·COOH (n = 0–8). For a given value of m, the plot of m.p. against n is a zig-zag curve in which the max. correspond to polyesters having consecutive even values of n; the plot of these max. passes through a min. Correspondingly, in the zig-zag plot of alcohol-solubility, the min. correspond to even n, and the plot of the min.

passes through a max. The results do not support the suggestion of Hill and Walker (*J. Polymer Science*, **3**, 609 (1948)) that the m.p. of polyesters for which *n* is even are determined only by the number of methylene groups in the repeating unit and not by their distribution between the glycol and acid residues. The effects attributable to the various components of the chain (–O–, –CO–, and –[CH₂]₍ₙ₎–) are discussed.

LXVIII— Polyesters formed by the same acids with diethylene glycol, triethylene glycol, and propane-1:2-diol are examined in the same way. They have much lower m.p. than the corresponding ethylene glycol polyesters (in many cases below − 40°c.), the m.p. of the triethylene glycol polyesters being lower than those of the diethylene glycol polyesters (lower m.p. is again associated with higher solubility); these effects are attributed to increase in the flexibility of the chains due to an increased proportion of –O– linkages. The "odd–even" effect and the tendency when *n* is even for the m.p. to pass through a min. as *n* increases are again very marked. The introduction of the methyl side-chain (polyesters derived from propane-1:2-diol) is similar in its effect on crystallinity, m.p., and solubility to the introduction of three or four ether linkages per repeating unit.   A. E. S.

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Water-dispersible Polyethylene. W. Spindler and W. Scheermesser.   BP 721,908
Polyethylene is dissolved at > 65°c. and the solution dispersed in an organic liquid of b.p. < 200°c. and which is miscible both with water and the solvent used for the polyethylene. The liquid phase is then separated from the dispersion, either mechanically or by spray-drying. This residue is a powder or paste which can be stirred directly with water to form a stable dispersion.
                    C. O. C.

Stabilising Nylon to Heat and Oxygen. DuP.
                    BP 722,724
Incorporation of a copper compound and an alkali metal halide, alkaline earth metal halide or ammonium halide in nylon stabilises it to heat and oxygen. The copper compound should be such that it dissolves in the nylon, e.g. Cu acetate.   C. O. C.

Solutions of Polyacrylonitrile. BrC.   BP 721,947
Acrylonitrile polymers can be dissolved readily in a mixture of nitric acid, water and an organic liquid which when hot is a solvent for polyacrylonitrile, there being 1–9 times by weight as much nitric acid as water.   C. O. C.

Heat Stabilisers for Halogen-containing Resins.
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Epoxyalkoxyaryl Resins—Coating Compositions, Fibres, Foils, etc. Koppers Co.   BP 721,149
Epoxyalkoxyaryl resins are prepared by condensing an aldehyde with hydrocarbon-substituted phenols having two positions, *o-* or *p-* to a phenolic group available for condensation with an aldehyde, e.g. *p*-cresol.

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Ion exchange resins containing several sulphonic acid groups are used as the catalyst for hardening polyepoxy compounds.

                    BP 721,151
The reaction products of halogeno epoxyalkanes with fusible chlorine-substituted phenolic-aldehyde resins are mobile liquids to hard solids. They are readily converted into insoluble, infusible, fire-retardant resins and may be used in preparing fibres, coating compositions, etc.

                    BP 721,152
Coating compositions are produced by condensing drying or semi-drying oil fatty acids or their polyhydric alcohol esters with the above epoxyalkoxy aryl resins.
                    BP 721,153
Incorporating an amine or cyanamide or their polymers or a polycarboxylic acid or anhydride into the above resins shortens the curing time.

                    BP 721,154
The heat and solvent resistance and mechanical properties of reactive H-containing resins suitable for making fibres and foils, e.g. viscose rayon, are improved by treating them with the above resins.   C. O. C.

Marbleising Plastic Sheet. Union Carbide & Carbon Corpn.   BP 720,922
Plastic sheeting having a coloured variegated marble appearance can be produced by placing short thin strips of coloured plastic on the offset roll of a conventional inverted L-type calender so that each strip is parallel to the nip. In the first nip, between the offset and the top rolls, the strips are embedded in the plastic and fuse into it to produce elongated streaks of colour. At the second nip, between the top and middle rolls, the coloured material is squeezed in a folding bank of plastic in a direction parallel to the nip so as to break up the coloured streaks and produce the marble effect. This folding bank is obtained by control of plastic temperature, difference in temperatures of the top and middle rolls, speed of calendering and the type of plastic employed
                    C. O. C.

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Flame-resistant Composition for Incorporation in Thermoplastic Polymers (III p. 191).
Aliphatic Azo Compounds—Polymerisation Catalysts (IV p. 195).
Terpolymers of Acrylonitrile, 1-Vinylimidazole and a Monomer containing the >C:C< Linkage (VI p. 198).

XIV— ANALYSIS; TESTING; APPARATUS

Modified High-frequency Apparatus for the Determination of Moisture in Solids— Determination of Moisture in Sodium Chloride and Ammonium Nitrate. F. W. Jensen, M. J. Kelly, and M. B. Burton. *Anal. Chem.*, **26**, 1716–1719 (Nov. 1954).
A high-frequency method is described which is based on the change in properties of a mixture of methanol and 1:4-dioxan due to the equilibrium extraction of moisture and salt from the solid. The apparatus is fully described and there is a circuit diagram. A precision of 0·02% was observed with the salts examined; within the range 0–2·5% moisture, moisture content is linearly related to current. It is considered that the method is applicable to other materials.   J. W. D.

Determination of Water by an Indirect Conductivity Method. C. K. Hancock and C. M. Hudgins. *Anal. Chem.*, **26**, 1738–1740 (Nov. 1954).
The conductivity of ethyl or methyl alcohol-acetone-water–NaCl systems varies almost linearly with the water content over the range 0–10% water. With ethanol the relationship is more nearly linear, but there is a corresponding decrease in sensitivity. The optimum acetone content is ∼ 30%.   J. W. D.

Theory of Chromatography. E. Glueckauf. *Trans. Faraday Soc.*, **51**, 34–44 (Jan. 1955).
The "theoretical plate" treatment for chromatographic separations is re-examined and the "discontinuous flow" treatment of Mayer and Tompkins replaced by a "continuous flow" model. The effects of finite width of feed band, purity of separated products, and non-equilibrium in particles are discussed for the purpose of predicting column performance.   W. R. M.
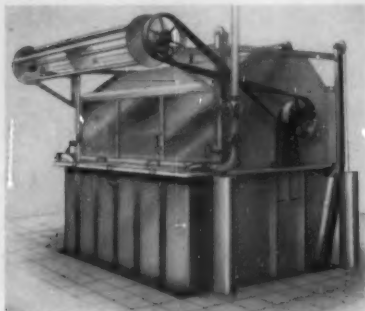
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